THE HONG KONG UNIVERSITY OF
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Final Report
for
Chemical Speciation of $PM_{2.5}$ Filter Samples

January 1 through December 31, 2013

(Tender Ref. 12-04384)

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1. Introduction

1.1 Background

The Environmental Protection Department of the Hong Kong Special Administration Region (HKEPD) proposed an updated Air Quality Objectives (AQOs) in January 2012. In the new AQOs, the concentration limit for 24-hour average $PM_{2.5}$ is set to be 75 $\mu g/m^3$ with 9 exceedance days allowed while the limit for annual average $PM_{2.5}$ is 35 $\mu g/m^3$. After a two-year legislative process, the new AQO was put in force on January 1, 2014.

In 2012, neither of the AQOs for $PM_{2.5}$ was achieved with the highest 24-hour average $PM_{2.5}$ concentration measured at Tung Chung (103 $\mu g/m^3$) and the highest annual average $PM_{2.5}$ concentration measured at Causeway Bay (42 $\mu g/m^3$). The Environment Bureau (ENB) has been implementing a wide range of measures locally to reduce the air pollution. In November 2012, the Hong Kong Special Administrative Region (HKSAR) and Guangdong Provincial Governments also endorsed a new set of regional emission reduction targets for the next 10 to 15 years, strengthening the collaboration between Guangdong and Hong Kong to deal with the regional air pollution.

In addition to the control measures that are being put forward, continuous monitoring of the air quality is necessary for the air pollution trend analysis. More specifically, the $PM_{2.5}$ chemical speciation studies would provide a better understanding on the nature and relative contributions of different emission sources that are responsible for the observed $PM_{2.5}$ levels in Hong Kong.

The HKEPD established a $PM_{2.5}$ chemical speciation network in 2000 and monitoring operations began in November, 2000. The HKEPD currently supports 6 sites as of the date of this report, which includes 4 collocated sites. The mass measurement data from the speciation network is used for identifying areas that meet or do not meet the new AQO criteria and supporting designation of an area as attainment or non-attainment. HKUST has been supporting HKEPD with the chemical speciation analysis of the $PM_{2.5}$ filter samples since 2011.

This report documents the $PM_{2.5}$ measurements and data validation for a twelve-month study from January to December 2013. The data were analyzed to characterize the composition and temporal and spatial variations of $PM_{2.5}$ concentrations in Hong Kong. Trends of $PM_{2.5}$ concentration and chemical composition were established by comparing the current study to the previous 12-month $PM_{2.5}$ studies since 2000. The monitoring data can further be used to explore the source contributions and investigate the hypotheses regarding the formation of $PM_{2.5}$ episodes.

1.2 Project Objectives and Task Description

The Environmental Central Facility (ENVF) at the Hong Kong University of Science and Technology (HKUST) assisted the Hong Kong Environmental Protection Department (HKEPD) in the analysis of $PM_{2.5}$ samples acquired over the course from January to December 2013. The objectives of this study were to:

- Determine the organic and inorganic composition of $PM_{2.5}$ and how it differs by season and proximity to different types of emission sources.
- Based on the ambient concentrations of certain tracer compounds, determine the contributions of different sources to $PM_{2.5}$ in Hong Kong.

- Investigate and understand the influences of meteorological/atmospheric conditions on $PM_{2.5}$ episodic events in Hong Kong.
- Establish inter-annual variability of $PM_{2.5}$ concentration and chemical composition in Hong Kong urban and rural areas.

The ENVF/HKUST team is responsible for:

- Receiving samples from the HKEPD and analyzing the filter samples for gravimetric mass and for an array of chemical constituents, including elements, soluble anions and cations, and carbonaceous material.
- Assembling validated sets of data from the analyses and preparing data files which will be entered into the HKEPD $PM_{2.5}$ speciation database.

1.3 Technical Approach

During the sampling period from January to December 2013, 24-hour $PM_{2.5}$ filter samples were acquired once every six days from the roadside-source-dominated Mong Kok (MK) Air Quality Monitoring Site (AQMS), the urban Central/Western (CW) and Tsuen Wan (TW) AQMSs, the new town Tung Chung (TC) and Yuen Long (YL) AQMSs, and the suburban Clear Water Bay (WB) Air Quality Research Site (AQRS) which is located on the campus of the Hong Kong University of Science and Technology. Three Partisol particle samplers (Rupprecht & Patachnick, Model 2025, Albany, NY) were used at MK, CW, WB, and TC sites while two Partisol samplers were placed at TW and YL sites to obtain $PM_{2.5}$ samples on both Teflon-membrane and QMA 47-mm filters. All sampled Teflon-membrane and QMA filters were analyzed for mass by gravimetric analysis by HKEPD’s contractor and then subjected to a suite of chemical analyses, including 1) determination of elements for atomic number ranging from 11 (Sodium) to 92 (Uranium) using Energy-Dispersive X-Ray Fluorescence (ED-XRF) Spectroscopy; 2) determination of chloride, nitrate, sulfate, sodium, ammonium, and potassium using Ion Chromatography (IC); and 3) determination of organic carbon (OC), elemental carbon (EC), total carbon (TC) and individual peaks for OC, EC, and pyrolyzed carbon on QMA filters using Thermal Optical Transmittance (TOT) and Thermal Optical Reflectance (TOR) by both NIOSH and IMPROVE protocols.

2. Sampling Network

2.1 Ambient $PM_{2.5}$ Monitoring Network

24-hour $PM_{2.5}$ filter samples were taken at five Air Quality Monitoring Stations (AQMSs) and one Air Quality Research Supersite (AQRS) in Hong Kong once every six days from January to December 2013. The six sampling sites are shown in Figure 1, representing roadside (MK), urban (CW and TW), new town (TC and YL), and suburban (WB) areas. The names, codes, locations, and descriptions of individual sites are listed in Table 1.

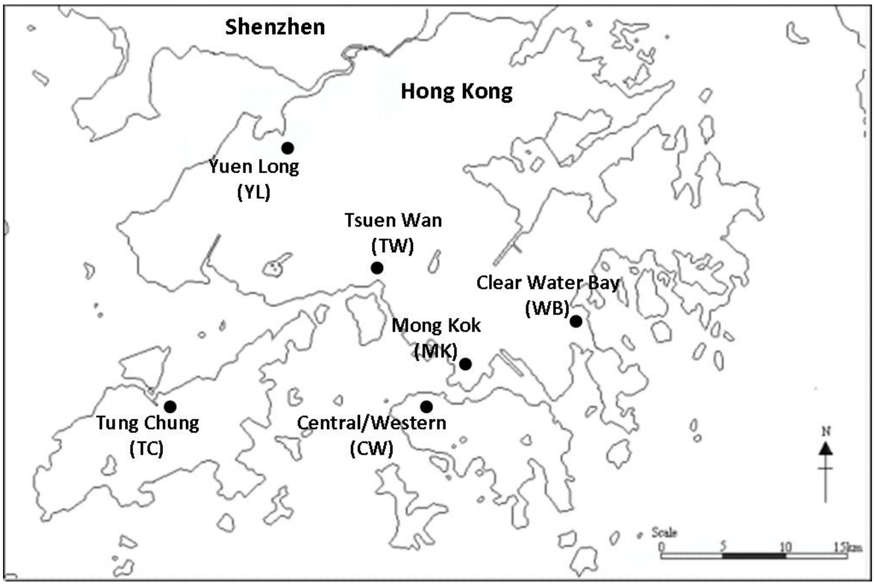


Figure 1. Monitoring sites in Hong Kong $PM_{2.5}$ speciation network.

Table 1. Descriptions of the monitoring sites.

Site Name	Site Code	Site Location	Site Description
Mong Kok	MK	Junction of Lai Chi Kok Road and Nathan Road, Kowloon	Urban roadside in mixed residential/commercial area with heavy traffic and surrounded by many tall buildings
Central/Western	CW	Rooftop of Sai Ying Pun Community Center, No. 2 High Street, Sai Ying Pun, Hong Kong	Urban, densely populated, residential site with mixed commercial development
Clear Water Bay	WB	Rooftop of a pump house next to Coastal Marine Lab, HKUST Campus, Clear Water Bay	Clean rural area with little residential and commercial development on the east coast of Sai Kung
Tung Chung	TC	Rooftop of Tung Chung Health Center, No. 6 Fu Tung Street, Lantau Island	Residential town, within 5 km southeast of HK International Airport
Tsuen Wan	TW	Rooftop of Princess Alexandra Community Center, 60 Tai Ho Road, New Territories	Urban, densely populated, residential site with mixed commercial and industrial developments. Located northwest of the MK site
Yuen Long	YL	Rooftop of Yuen Long District Branch Office Building, 269 Castle Peak Road, New Territories	Residential town, about 15 km southwest of Shenzhen

2.2 Ambient $PM_{2.5}$ Measurements

A total of 16 Partisol samplers were employed to obtain $PM_{2.5}$ samples around Hong Kong. The detailed arrangement of the samplers is described in Table 2.

Table 2. Arrangement of the Partisol samplers in the monitoring sites.

Location	No. of Samplers	Collocated Samples
MK AQMS	3	Teflon Filters
CW AQMS	3	Teflon Filters
WB AQRS	3	QMA Filters
TC AQMS	3	QMA Filters
TW AQMS	2	
YL AQMS	2	

Each Partisol sampler was equipped with an Andersen $PM_{2.5}$ inlet with Very Sharp Cut Cyclone (VSCC). The samplings were conducted at a flow rate of 16.7 L/min. At this flow rate, a nominal volume of approx. 24.0 m^3 of ambient air would be sampled over a 24-hour period. The Partisol samplers were configured to take either a Teflon-membrane filter or a QMA filter. For this study, the following filters were chosen: 1) Whatman (Clifton, NJ, USA),

$PM_{2.5}$ membrane, PTFE, 46.2 mm with support ring (#7592204); and 2) Pall Life Sciences (Ann Arbor, MI, USA), 2500QAT-UP, 47 mm, Tissuquartz^{TM} filters (#7202).

The Partisol samplers were operated and maintained by HKEPD's contractor, AECOM Asia Company Limited, throughout the study period. The ENVF/HKUST team was responsible for pre- and post-sampling procedures required for quality assurance and sample preservation. ENVF/HKUST team was also responsible for the gravimetric analysis on both filter types before and after sampling.

The collected Teflon-membrane filters were used for gravimetric analysis for $PM_{2.5}$ mass concentrations and elemental analysis (for more than 40 elements with atomic number ranging from 11 to 92) by X-Ray Fluorescence (XRF) [Watson et al., 1999]. The collected QMA filters were analyzed for mass concentrations by gravimetry, for carbon contents by multiple thermal evolution methods, and for chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), water-soluble sodium (Na^+), ammonium (NH_4^+), and water-soluble potassium (K^+) by ion chromatography.

A major uncertainty in determining carbon concentrations lies in the differentiation of organic and elemental carbon during analysis. EC has been defined as the carbon that evolves after the detected optical signal attains the value it had prior to commencement of heating and the rest of the carbon is considered to be OC [Chow et al., 1993; Birch and Cary, 1996]. The split of OC and EC in the thermal analysis depends on several parameters including temperature setpoints, temperature ramping rates, residence time at each setpoint, combustion atmospheres, and optical signal used. Heating in an inert atmosphere causes certain OC to pyrolyze or char, inflating the EC in the sample. The extent of pyrolysis is affected by different thermal/temperature protocols. A laser is used to overcome this problem by monitoring changes in filter darkness during the thermal evolution process by detecting either filter transmittance (thermal/optical transmittance [TOT] method) or reflectance (thermal/optical reflectance [TOR] method). However, this introduces another problem of inner/near-surface filter pyrolysis. It is found that pyrolysis occurs both within filter and on the filter surface. TOT method measures light transmittance which goes through the filter and is more likely influenced by the inner filter char while TOR method is more influenced by the charring of near-surface deposit.

In this study, two analytical protocols - National Institute of Occupational Safety and Health (NIOSH 5040) protocol coupled with TOT method for charring correction, and the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol coupled with TOR method for charring correction are employed to analyze the QMA filters. Table 3 shows the temperature programs of the NIOSH and IMPROVE protocols. Results obtained with the two protocols are compared and evaluated in Section 3.3.4.

Table 3. Temperature programs of the IMPROVE and the NIOSH protocols.

Methods' carrier gas	**Carbon fraction**	**NIOSH_TOT temp, time**	**IMPROVE_TOR* temp, time**
He purge		25°C, 10 s	25°C, 10 s
He-1	OC1	310°C, 80 s	120°C, 180 s
He-2	OC2	475°C, 60 s	250°C, 180 s
He-3	OC3	615°C, 60 s	450°C, 180 s
He-4	OC4	870°C, 90 s	550°C, 180 s
He-5		Cool oven	-
O_2 / He-1	EC1	550°C, 45 s	550°C, 240 s
O_2 / He-2	EC2	625°C, 45 s	700°C, 210 s
O_2 / He-3	EC3	700°C, 45 s	850°C, 210 s
O_2 / He-4	EC4	775°C, 45 s	
O_2 / He-5	EC5	850°C, 45 s	
O_2 / He-6	EC6	870°C, 45 s	

* The IMPROVE temperature program was used for measurements reported in this work. Another related temperature protocol, termed IMPROVE_A, is typically adopted on DRI Model 2001 carbon analyzers. The IMPROVE_A temperature protocol defines temperature plateaus of 140 °C for OC1, 280 °C for OC2, 480 °C for OC3, and 580 °C for OC4 in a helium (He) carrier gas and 580 °C for EC1, 740 °C for EC2, and 840 °C for EC3 in a 98% He/2% oxygen (O_2) carrier gas [Chow et al., 2007]. These temperatures used with the new hardware in DRI Model 2001 better match the sample temperatures experienced in the analysis using the IMPROVE protocol on the previous models of DRI analyzers.

2.3 Sample Delivery and Filter Conditions

A total of 1104 samples including 552 pieces of Teflon filters and 552 pieces of QMA filters were received. The sampling dates on which the samples were collected were summarized in Table 4 and there were 62 sampling events taken place in 2013.

Table 4. Valid sampling dates for the $PM_{2.5}$ samples in 2013 (Tender Ref. 12-04384).

January	February	March	April	May	June
130112 w/BLK 130118 130124 130130	130205 130211 130217 130223	130301 130307 w/BLK 130313 130319 130325 130331	130406 130412 130418 130424 130430	130506 w/BLK 130512 130518 130524 130530	130605 130611 130617 130623 130629
July	**August**	**September**	**October**	**November**	**December**
130705 w/BLK 130711 130717 130723 130729	130804 130810 130816 130822 130828	130903 w/BLK 130909 130911 130915 130921 130925 130927	131003 131009 131015 131021 131027	131102 w/BLK 131108 131114 131120 131126	131202 131208 131214 131217 131220 131226 w/BLK

During the Level I data validation, 7 filter samples were identified to be invalid. The corresponding sample IDs, filter IDs, and a brief account for invalidating these samples is provided in Table 5.

Table 5. List of invalid filter samples in 2013 (Tender Ref. 12-04384).

Sample ID	Filter ID	$PM_{2.5}$ Mass (Teflon), µg/m^3	$PM_{2.5}$ Mass (QMA), µg/m^3	Remark
MK130406SF02T	T0010137	- / 28.96*	36.54	Power failure
MK130816SF02T	T0010321	- / 21.00	33.00	Power failure
MK130903PF03T	T0010362	21.08 / -	19.92	Power failure
MK130909SF01Q	Q0020224	28.25 / 28.67	6.13	Q mass extremely low
CW130418SF02T	T0010155	21.04 / 20.50	29.34	Filter broken
CW130530SF01Q	Q0020075	9.50 / 9.46	-	Power failure
CW131208SF02T	T0010530	56.83 / 55.38	56.42	Longer sampling duration
TW130915SF01Q	Q0020241	21.79	1.50	Q mass extremely low

*For MK and CW sites, the PM mass data obtained from Teflon samples were presented as mass from channel 2 (SF02T) / mass from channel 3 (PF03T).

For the 4 sampling dates on which the channel 2 Teflon filter samples (SF02T) were identified invalid, the collocated samples (i.e., MK130406PF03T, MK130816PF03T, CW130418PF03T and CW131208PF03T, respectively) were used in Level II Data Validation and identified as valid.

For the 2 QMA filter samples collected in MK on September 9, 2013 and in TW on September 15, 2013, respectively, sampling log checking and visual checking on the samples were done right after the weighing session ended. Nothing abnormal was found in the log sheet and the filters seemed to be in good conditions with the degree of blackness similar to those on the collocated Teflon filters. Carbon analysis was subsequently performed. The total carbon (TC) concentration of MK130909SF01Q was 11.8 μgC/m^3, which was comparable to the concentration levels observed in MK on other days. The TC concentration of TW130915SF01Q was 8.2 μgC/m^3. It was compared to a collocated QMA filter sample which was collected by an RAAS multichannel sampler operated by the HKUST team in the same sampling site. The relative difference of the analytical results was approx. 6%. Therefore, these two samples were continued with Level II Data Validation and identified as valid. Invalid flags were put onto the PM mass data obtained from the QMA filters and it was suggested that fiber/fragment lost from the QMA filters could explain the large discrepancy between the QMA mass and Teflon mass.

Since there was only one QMA filter collected in CW site and CW130530SF01Q was flagged as invalid due to the power failure of the sampler, the chemical information was incomplete for CW on May 30, 2013.

3. Database and Data Validation

3.1 Data File Preparation

An electronic database on analytical results is established for Hong Kong $PM_{2.5}$ data archive. Detailed data processing and data validation are documented in Section 3.3. The data are available on Compact Disc in the format of Microsoft Excel spreadsheets for convenient distribution to data users. The contents of the final data files are listed in Table 6.

Table 6. Summary of data files for the $PM_{2.5}$ study (EPD Tender Ref. 12-04384) in Hong Kong.

Category	Database File	File Description
I. DATABASE DOCUMENTATION		
	12-04384_ID.xls	Defines the field sample names, measurement units, and formats used in the database file
II. MASS AND CHEMICAL DATA		
	12-04384_PM2.5.xls	Contains $PM_{2.5}$ mass data and chemical data for samples collected by Partisol samplers at six sites once every six days during January to December 2013
III. DATABASE VALIDATION		
	12-04384_FLAG.xls	Contains both field sampling and chemical analysis data validation flags

3.2 Measurement and Analytical Specifications

The measurement/analysis methods are described in Section 2 and every measurement consists of 1) a value; 2) a precision (uncertainty), and 3) a validity. The values are obtained by different analysis methods. The precisions are estimated through standard testing, blank analysis, and replicate analysis. The validity of each measurement is indicated by appropriate flagging in the data base, while the validity of chemical analysis results are evaluated by data validations described in Section 3.3.

A total of 69 sets of ambient $PM_{2.5}$ samples were received during this study and submitted for comprehensive chemical analyses. These 69 sets of samples include 7 sets of field blanks. 4

out of 6 sites conducted collocated sampling and the collocated samples were used for data validation purpose. 984 out of the 992 $PM_{2.5}$ samples acquired are considered valid after data validation and final review.

3.2.1 Precision Calculations and Error Propagation

Measurement precisions are propagated from precisions of volumetric measurements, chemical composition measurements, and field blank variability using the methods of Bevington [1969] and Watson et al. [2001]. The following equations are used to calculate the prevision associated with filter-based measurements:

$$C_i = \frac{M_i - B_i}{V} \tag{1}$$

$$V = Q \times T \tag{2}$$

$$B_i = \frac{1}{n}\sum_{o=1}^{n} B_{io} \qquad for\ B_i > \sigma_{B_i} \tag{3}$$

$$B_i = 0 \qquad for\ B_i < \sigma_{B_i} \tag{4}$$

$$\sigma_{B_i} = STD_{B_i} = \left[\frac{i}{n-1}\sum_{o=1}^{n}\left(B_{io} - B_i\right)^2\right]^{\frac{1}{2}} \qquad for\ STD_{B_i} > SIG_{B_i} \tag{5}$$

$$\sigma_{B_i} = SIG_{B_i} = \left[\frac{i}{n}\sum_{o=1}^{n}\left(\sigma_{B_{io}}\right)^2\right]^{\frac{1}{2}} \qquad for\ STD_{B_i} \le SIG_{B_I} \tag{6}$$

$$\sigma_{C_i} = \left[\frac{\sigma_{M_i}^2 + \sigma_{B_i}^2}{V^2} + \frac{\sigma_V^2\left(M_i - B_i\right)^2}{V^4}\right]^{\frac{1}{2}} \tag{7}$$

$$\sigma_{RMSi} = \left(\frac{1}{n}\sum_{o=1}^{n}\sigma_{C_i}^2\right)^{\frac{1}{2}} \tag{8}$$

$$\frac{\sigma_V}{V} = 0.05 \tag{9}$$

Where:

B_i = average amount of species i on field blanks

B_{io} = the amount of species i found on field blank o

C_i = the ambient concentration of species i

Q = flow rate throughout sampling period

M_i = amount of species i on the substrate

N = total number of samples in the sum

SIG_{Bi} = the root mean square error (RMSE), the square root of the averaged sum of the squared σ_{Bio}

STD_{Bio} = standard deviation of the blank

σ_{Bi} = blank precision for species i

σ_{Bio} = precision of the species i found on field blank j

σ_{Ci} = propagated precision for the concentration of species i

σ_{Mi} = precision of amount of species i on the substrate

σ_{RMSi} = root mean square precision for species i

σ_{V} = precision of sample volume

T = sample duration

V = volume of air sampled

The uncertainty of the measured value and the average uncertainty of the field blanks for each species are used to propagate the overall precision for each blank subtracted concentration value. The final value is propagated by taking the square root of the sum of the squares of the calculated uncertainty and the average field blank uncertainty for each measurement.

3.2.2 Analytical Specifications

The concentrations of field blanks collected during the study are summarized in Table 7 in the unit of µg/filter.

Blank precisions (σ_{Bi}) are defined as the higher value of the standard deviation of the blank measurements, STD_{Bi}, or the square root of the averaged squared uncertainties of the blank concentrations, SIG_{Bi}. If the average blank for a species was less than its precision, the blank was set to zero (Eqn 4).

The precisions (σ_{Mi}) were determined from duplicate analysis of samples. When duplicate sample analysis is made, the range of results, R, is nearly as efficient as the standard deviation since two measures differ by a constant (1.128s = R where s represents the precision).

Table 7. Field blank concentrations of $PM_{2.5}$ samples collected at MK, CW, WB, TC, TW, and YL sites during the study period in Hong Kong.

	Amounts in μg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD_{Bi})**	**Root Mean Squared Blank Precision (SIG_{Bi})**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B_i)**
Na^+	56	1.122	0.318	1.122	-0.935	0.000
NH_4^+	56	0.413	0.202	0.413	-0.548	0.000
K^+	56	0.846	0.578	0.846	-0.604	0.000
Cl^-	56	0.539	0.619	0.619	1.038	1.038
NO_3^-	56	0.889	1.934	1.934	2.692	2.692
SO_4^{2-}	56	0.672	1.514	1.514	1.570	1.570
OC1_TOR	56	0.525	2.429	2.429	0.660	0.000
OC2_TOR	56	2.028	2.796	2.796	7.970	7.970
OC3_TOR	56	1.542	2.682	2.682	5.708	5.708
OC4_TOR	56	0.626	2.460	2.460	1.277	0.000
OC_TOR	56	4.780	3.321	4.780	18.339	18.339
OC_TOT	56	5.016	3.366	5.016	19.225	19.225
PyC_TOR	56	1.428	2.533	2.533	2.724	2.724
PyC_TOT	56	0.413	2.420	2.420	0.470	0.000
EC1_TOR	56	0.218	2.398	2.398	0.041	0.000
EC2_TOR	56	0.368	2.400	2.400	0.087	0.000
EC3_TOR	56	0.229	2.399	2.399	0.051	0.000
EC_TOR	56	0.764	2.405	2.405	0.179	0.000
EC_TOT	56	1.443	2.411	2.411	0.283	0.000
TC	56	4.815	3.330	4.815	18.518	18.518
Na	56	0.1040	0.3890	0.3890	0.0554	0.0000
Mg	56	0.1802	1.7686	1.7686	0.4667	0.0000
Al	56	0.1130	0.6040	0.6040	0.1598	0.0000
Si	56	0.1823	0.6178	0.6178	-0.0351	0.0000
P	56	0.0233	0.0480	0.0480	-0.0176	0.0000
S	56	0.0012	0.0823	0.0823	0.0003	0.0000
Cl	56	0.0199	0.0900	0.0900	0.0107	0.0000

	Amounts in µg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD_{Bi})**	**Root Mean Squared Blank Precision (SIG_{Bi})**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B_i)**
K	56	0.0187	0.0404	0.0404	0.0132	0.0000
Ca	56	0.0306	0.1178	0.1178	-0.0400	0.0000
Sc	56	0.0531	0.4889	0.4889	0.1718	0.0000
Ti	56	0.0067	0.0352	0.0352	0.0052	0.0000
V	56	0.0061	0.0137	0.0137	-0.0049	0.0000
Cr	56	0.0099	0.0210	0.0210	0.0082	0.0000
Mn	56	0.0391	0.1207	0.1207	0.0569	0.0000
Fe	56	0.0536	0.1283	0.1283	-0.0641	0.0000
Co	56	0.0081	0.0258	0.0258	-0.0003	0.0000
Ni	56	0.0164	0.0271	0.0271	0.0119	0.0000
Cu	56	0.0361	0.0478	0.0478	0.0243	0.0000
Zn	56	0.0295	0.2049	0.2049	0.0055	0.0000
Ga	56	0.0262	0.0781	0.0781	0.0334	0.0000
Ge	56	0.0194	0.0847	0.0847	-0.0152	0.0000
As	56	0.0000	0.0066	0.0066	0.0000	0.0000
Se	56	0.0000	0.0343	0.0343	0.0000	0.0000
Br	56	0.0153	0.0282	0.0282	-0.0103	0.0000
Rb	56	0.0105	0.0508	0.0508	-0.0003	0.0000
Sr	56	0.0160	0.0223	0.0223	-0.0126	0.0000
Y	56	0.0074	0.0993	0.0993	-0.0039	0.0000
Zr	56	0.0349	0.0828	0.0828	0.0099	0.0000
Nb	56	0.0340	0.0738	0.0738	-0.0470	0.0000
Mo	56	0.0324	0.0943	0.0943	-0.0644	0.0000
Rh	56	0.0511	0.1851	0.1851	0.0553	0.0000
Pd	56	0.0572	0.0593	0.0593	-0.1196	0.0000
Ag	56	0.0399	0.1098	0.1098	0.0209	0.0000
Cd	56	0.0495	0.1694	0.1694	0.0322	0.0000
In	56	0.0651	0.2447	0.2447	-0.0195	0.0000
Sn	56	0.0638	0.2381	0.2381	-0.0734	0.0000
Sb	56	0.0650	0.2752	0.2752	0.0217	0.0000
Te	56	0.0978	0.2440	0.2440	-0.0610	0.0000
I	56	0.1219	1.5365	1.5365	0.1045	0.0000

	Amounts in µg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD_{Bi})**	**Root Mean Squared Blank Precision (SIG_{Bi})**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B_i)**
Cs	56	0.2038	2.2266	2.2266	0.5369	0.0000
Ba	56	0.2389	2.7106	2.7106	0.9826	0.0000
La	56	0.2706	0.6785	0.6785	0.8899	0.8899
Ce	56	0.0206	0.0731	0.0731	0.0204	0.0000
Sm	56	0.0298	0.2215	0.2215	0.0367	0.0000
Eu	56	0.0639	0.0640	0.0640	-0.0296	0.0000
Tb	56	0.0374	0.5426	0.5426	0.0188	0.0000
Hf	56	0.1164	0.3205	0.3205	0.1298	0.0000
Ta	56	0.0860	0.6066	0.6066	0.0513	0.0000
W	56	0.2159	0.1979	0.2159	0.3633	0.3633
Ir	56	0.0264	0.0176	0.0264	-0.0554	0.0000
Au	56	0.0337	0.0070	0.0337	0.0191	0.0000
Hg	56	0.0011	0.0861	0.0861	0.0001	0.0000
Tl	56	0.0312	0.0996	0.0996	0.0131	0.0000
Pb	56	0.0335	0.1092	0.1092	-0.0199	0.0000
U	56	0.0453	0.0168	0.0453	-0.0710	0.0000

The analytical specifications for the 24-hour $PM_{2.5}$ measurements obtained during the study are summarized in Table 8. Limits of detection (LOD) and limits of quantitation (LOQ) are given. The LOD of an analyte may be described as that concentration which gives an instrument signal significantly different from the “blank” or “background” signal. In this study LOD is defined as the concentration at which instrument response equals three times the standard deviation of the concentrations of low level standards. As a further limit, the LOQ is regarded as the lower limit for precise quantitative measurements and is defined as a concentration corresponding to ten times the standard deviation of the concentrations of low level standards. The LOQs should always be equal to or larger than the analytical LODs and it was the case for all the chemical compounds listed in Table 7. Both the LODs and LOQs are in the unit of µg/filter assuming the effective sampling area of the 47-mm filter is 11.98 cm^2.

Table 8. Analytical specifications of 24-hour $PM_{2.5}$ measurements at MK, CW, WB, TC, TW, and YL sites during the study period in Hong Kong.

Species	Analytical Method	LOD (µg/filter)	LOQ (µg/filter)	No. of valid Values	No. > LOD	% > LOD	No. > LOQ	% > LOQ
Na^+	IC	0.074	0.246	495	489	99%	483	98%
NH_4^+	IC	0.049	0.162	495	495	100%	495	100%
K^+	IC	0.143	0.476	495	471	95%	373	75%
Cl^-	IC	0.153	0.510	495	460	93%	237	48%
NO_3^-	IC	0.480	1.601	495	495	100%	401	81%
SO_4^{2-}	IC	0.377	1.256	495	495	100%	495	100%
OC1_TOR	TOR	0.035	0.117	495	264	53%	27	5%
OC2_TOR	TOR	0.090	0.299	495	495	100%	493	100%
OC3_TOR	TOR	0.113	0.376	495	495	100%	495	100%
OC4_TOR	TOR	0.078	0.261	495	495	100%	479	97%
OC_TOR	TOR	0.405	1.350	495	495	100%	495	100%
OC_TOT	TOT	3.188	10.626	495	495	100%	495	100%
PyC_TOR	TOR	0.228	0.760	495	472	95%	386	78%
PyC_TOT	TOT	1.046	3.486	495	471	95%	420	85%
EC1_TOR	TOR	0.133	0.442	495	492	99%	454	92%
EC2_TOR	TOR	0.087	0.289	495	495	100%	491	99%
EC3_TOR	TOR	0.052	0.175	495	475	96%	357	72%
EC_TOR	TOR	0.044	0.146	495	495	100%	495	100%
EC_TOT	TOT	0.008	0.027	495	490	99%	490	99%
TC	TOR	0.410	1.367	495	495	100%	495	100%
Na	XRF	0.3012	1.0040	491	491	100%	486	99%
Mg	XRF	1.3576	4.5253	491	486	99%	292	59%
Al	XRF	0.5442	1.8139	491	489	100%	382	78%
Si	XRF	0.6258	2.0860	491	482	98%	407	83%
P	XRF	0.0531	0.1770	491	456	93%	356	73%
S	XRF	0.0822	0.2740	491	491	100%	491	100%
Cl	XRF	0.0881	0.2937	491	479	98%	390	79%
K	XRF	0.0378	0.1260	491	491	100%	491	100%
Ca	XRF	0.1273	0.4242	491	491	100%	487	99%
Sc	XRF	0.4442	1.4807	491	0	0%	0	0%
Ti	XRF	0.0343	0.1144	491	478	97%	382	78%

Species	**Analytical Method**	**LOD (µg/filter)**	**LOQ (µg/filter)**	**No. of valid Values**	**No. > LOD**	**% > LOD**	**No. > LOQ**	**% > LOQ**
V	XRF	0.0143	0.0478	491	490	100%	486	99%
Cr	XRF	0.0199	0.0664	491	319	65%	137	28%
Mn	XRF	0.1087	0.3625	491	431	88%	186	38%
Fe	XRF	0.1400	0.4665	491	489	100%	485	99%
Co	XRF	0.0259	0.0862	491	26	5%	0	0%
Ni	XRF	0.0252	0.0840	491	491	100%	340	69%
Cu	XRF	0.0439	0.1462	491	490	100%	428	87%
Zn	XRF	0.2036	0.6785	491	467	95%	401	82%
Ga	XRF	0.0676	0.2254	491	12	2%	0	0%
Ge	XRF	0.0876	0.2920	491	7	1%	0	0%
As	XRF	0.0066	0.0221	491	219	45%	207	42%
Se	XRF	0.0000	0.0000	491	5	1%	5	1%
Br	XRF	0.0343	0.1145	491	424	86%	330	67%
Rb	XRF	0.0309	0.1030	491	131	27%	10	2%
Sr	XRF	0.0508	0.1692	491	191	39%	19	4%
Y	XRF	0.0247	0.0823	491	25	5%	0	0%
Zr	XRF	0.1001	0.3337	491	57	12%	0	0%
Nb	XRF	0.0799	0.2664	491	1	0%	0	0%
Mo	XRF	0.0852	0.2840	491	1	0%	0	0%
Rh	XRF	0.1096	0.3652	491	71	14%	0	0%
Pd	XRF	0.1694	0.5647	491	0	0%	0	0%
Ag	XRF	0.0897	0.2989	491	30	6%	0	0%
Cd	XRF	0.1039	0.3463	491	44	9%	0	0%
In	XRF	0.1582	0.5273	491	0	0%	0	0%
Sn	XRF	0.2488	0.8294	491	124	25%	15	3%
Sb	XRF	0.2602	0.8673	491	22	4%	0	0%
Te	XRF	0.2688	0.8961	491	1	0%	0	0%
I	XRF	0.2624	0.8745	491	97	20%	0	0%
Cs	XRF	1.4810	4.9368	491	0	0%	0	0%
Ba	XRF	1.8622	6.2074	491	46	9%	0	0%
La	XRF	2.0885	6.9616	491	0	0%	0	0%
Ce	XRF	0.0464	0.1548	491	32	7%	0	0%
Sm	XRF	0.0684	0.2279	491	149	30%	0	0%
Eu	XRF	0.2124	0.7078	491	11	2%	0	0%
Tb	XRF	0.0696	0.2321	491	116	24%	30	6%

Species	Analytical Method	LOD (µg/filter)	LOQ (µg/filter)	No. of valid Values	No. > LOD	% > LOD	No. > LOQ	% > LOQ
Hf	XRF	0.5387	1.7956	491	0	0%	0	0%
Ta	XRF	0.2873	0.9577	491	67	14%	0	0%
W	XRF	0.5937	1.9789	491	0	0%	0	0%
Ir	XRF	0.1014	0.3379	491	0	0%	0	0%
Au	XRF	0.0285	0.0951	491	23	5%	1	0%
Hg	XRF	0.0000	0.0000	491	0	0%	0	0%
Tl	XRF	0.0861	0.2870	491	1	0%	0	0%
Pb	XRF	0.0970	0.3234	491	358	73%	294	60%
U	XRF	0.1132	0.3773	491	0	0%	0	0%

The number of reported concentrations for each species and number of reported concentrations greater than the LODs and LOQs are also summarized in Table 8. For the 495 valid filter samples, major ions (including chloride, nitrate, sulfate, ammonium, soluble sodium, and soluble potassium), organic carbon, elemental carbon, sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn) were detected (> LOD) in almost all the samples (more than 90%). Several transition metals (e.g. Sc, Co, Y, Zr, Nb, Mo, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Ir, Au, Hg, and U) were not detected in most of the samples (less than 15%). Species from motor vehicle exhaust such as Br and Pb were detected in 86% and 73% of the samples, respectively. V and Ni, which are residual-oil-related species, were both detected in all the samples. This is typical for urban and suburban sites in most regions. Toxic species emitted from industrial sources, such as Cd and Hg, were not detected (9% and 0% of the samples, respectively). Soil-dust-related species, including Al, Si, Ca, Ti, and Fe, were found above the LODs in more than 97% of the samples and above the LOQs in more than 78% of the samples.

In general, the analytical specifications shown in Table 8 suggest that the $PM_{2.5}$ samples collected during the study period possess adequate loading for chemical analysis. The detection limits of the selected analytical methods were sufficiently low to establish valid measurements with acceptable precision.

3.3 Data Validation

Three levels of data validation were conducted to the data acquired from the study.

Level I data validation: 1) flag measurements for deviations from procedures; 2) identify and remove invalid values and indicate the reasons for invalid sampling, and 3) estimate precisions from replicate and blank analyses.

Level II data validation examines internal consistency tests among different data and attempts to resolve discrepancies based on known physical relationships between variables: 1) compare a sum of chemical species to mass concentrations; 2) compare measurements from different methods; 3) compare collocated measurements; 4) examine time series from different sites to identify and investigate outliers, and 5) prepare a data qualification statement.

Level III data validation is part of the data interpretation process and should identify unusual values including: 1) extreme values; 2) values which would otherwise normally track the values of other variables in a time series, and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern. External consistency tests are used to identify values in the data set which appear atypical when compared to other data sets. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If nothing unusual is found upon tracing the path of the measurement, the value would be assumed to be a valid result of an environmental cause.

Level I data validation was performed and the validation flags and comments are stated in the database as documented in Section 3.1. Level II validation tests and results are described in the following subsections including 1) sum of chemical species versus $PM_{2.5}$ mass; 2) physical and chemical consistency; 3) anion/cation balance; 4) reconstructed versus measured mass; 5) carbon measurements by different thermal/optical methods, and 6) collocated measurement comparison. For Level III data validation, parallel consistency tests were applied to data sets from the same population (e.g., region, period of time) by different data analysis approaches. Collocated samples collected at four out of the six sampling sites were examined. Comparison of $PM_{2.5}$ mass concentrations obtained from gravimetric analysis and from 24-hr average continuous measurements were also conducted. The level III data validation continues for as long as the database is maintained. For Level II/III data validation in this study, correlations and linear regression statistics were performed on the valid data set and scatter plots were generated for better comparison.

3.3.1 Sum of Chemical Species versus $PM_{2.5}$ Mass

The sum of the individual chemical concentrations determined in this study for $PM_{2.5}$ samples should be less than or equal to the corresponding mass concentrations obtained from gravimetric measurements. The chemical species include those that were quantified on both Teflon-membrane filters and quartz fiber filters. To avoid double counting, chloride (Cl^-), total potassium (K), soluble sodium (Na^+), and sulfate (SO_4^{2-}) are included in the sum while total sulfur (S), total chlorine (Cl), total sodium (Na), and soluble potassium (K^+) are excluded. Carbon concentration is represented by the sum of organic carbon and elemental carbon. Unmeasured ions, metal oxides, or hydrogen and oxygen associated with organic carbon are not counted into the measured concentrations.

The sum of chemical species was plotted against the measured $PM_{2.5}$ mass on Teflon filters for each of the individual sites in Figure 2. Linear regression analysis results and the average ratios of Y over X are both shown in Table 9 for comparison. Each plot contains a solid line indicating the slope with intercept and a dashed 1:1 line. Measurement uncertainties associated with the x- and y-axes are shown and the uncertainties of the $PM_{2.5}$ mass data were assumed to be 5% of the concentrations.

A strong correlation ($R^2 = 0.99$) was found between the sum of measured species and mass with a slope of 0.808 ± 0.005. The average Y/X ratios indicate that approximately 77 - 91% of the $PM_{2.5}$ mass can be explained by the measured chemical species.

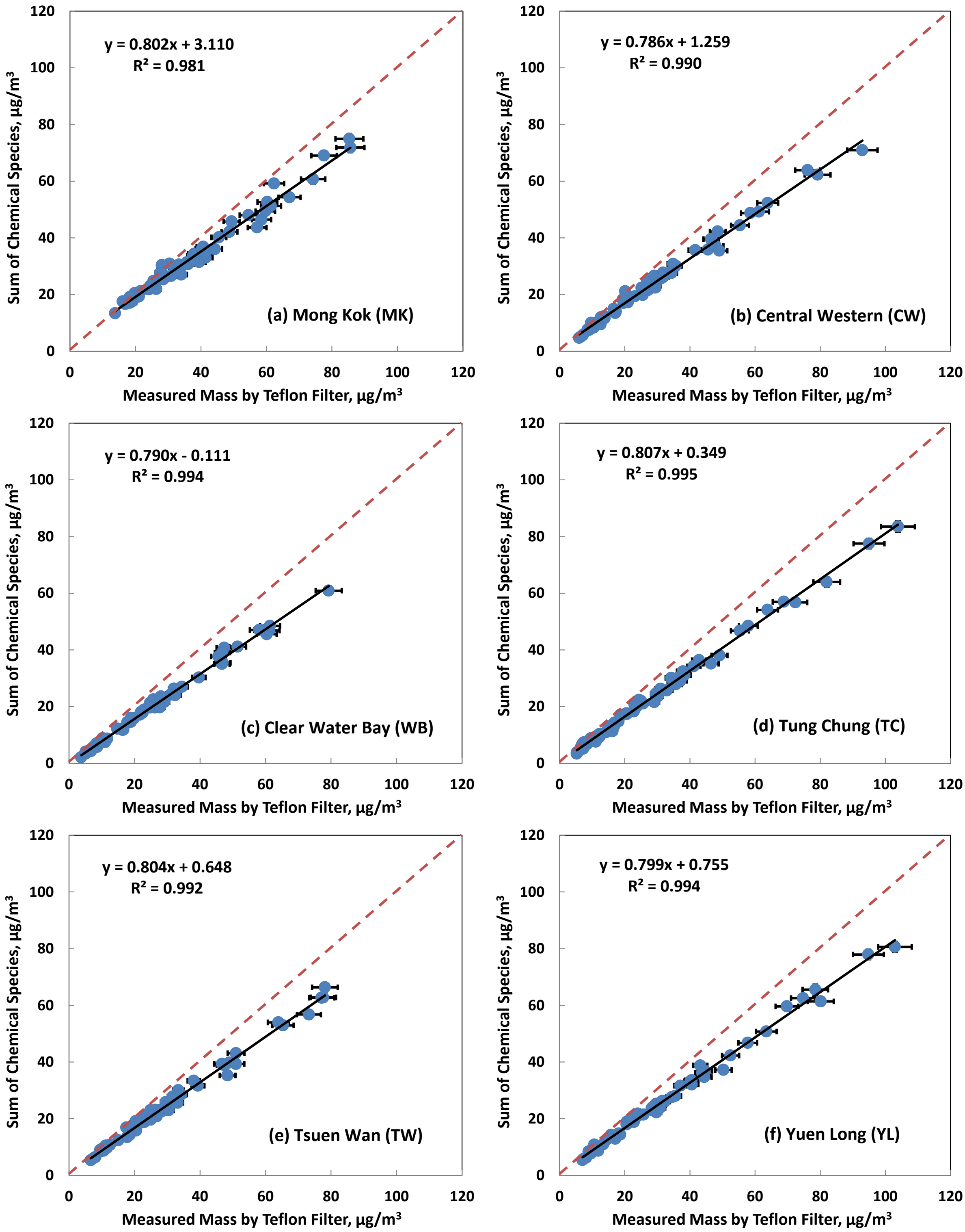


Figure 2. Scatter plots of sum of measured chemical species versus measured mass on Teflon filter for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 9. Statistics analysis of sum of measured chemical species versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Slope	0.802 (±0.015)	0.786 (±0.010)	0.790 (±0.008)	0.807 (±0.007)	0.804 (±0.009)	0.799 (±0.008)	0.808 (±0.005)
Intercept	3.110 (±0.592)	1.259 (±0.350)	-0.111 (±0.256)	0.349 (±0.256)	0.648 (±0.328)	0.755 (±0.300)	0.721 (±0.171)
R^2	0.981	0.990	0.994	0.995	0.992	0.994	0.987
AVG mass	36.72	28.99	26.08	28.59	29.50	31.01	30.15
AVG sum	32.56	24.05	20.48	23.43	24.38	25.54	25.08
AVG sum/mass	0.909 (±0.074)	0.843 (±0.061)	0.774 (±0.058)	0.820 (±0.064)	0.835 (±0.051)	0.834 (±0.054)	0.836 (±0.072)

Limits used for identifying reconstructed mass outliers are referring to those in Speciation Trends Network (STN) program suggested by USEPA [2012] and are listed as follows,

Lower Limit: [Sum of Chemical Species]/[Measured Mass] < 0.60

Upper Limit: [Sum of Chemical Species]/[Measured Mass] > 1.32

Based on these criteria, only WB130717 was identified as the outlier with the ratio being 0.56. However, it was also stated in the USEPA guidance document that this criteria does NOT apply to the samples with lower level of filter loading. Further checking confirmed that the lowest $PM_{2.5}$ concentration (3.75 $\mu g/m^3$) was found at WB site on July 17, 2013. Therefore, this sample will not be flagged.

3.3.2 Physical and Chemical Consistency

Measurements of chemical species concentrations conducted by different methods are compared. Physical and chemical consistency tests include: 1) sulfate (SO_4^{2-}) versus total sulfur (S); 2) soluble potassium (K^+) versus total potassium (K), and 3) chloride (Cl^-) versus total chlorine (Cl).

3.3.2.1 Water-Soluble Sulfate (SO_4^{2-}) versus Total Sulfur (S)

SO_4^{2-} is measured by ion chromatography (IC) on QMA filters and total S is measured by X-Ray Fluorescence (XRF) on Teflon filters. The theoretical ratio of SO_4^{2-} to S is 3, based on their molecular weights and assuming all of the sulfur is present as SO_4^{2-}. Since SO_4^{2-} and total S are collected on different filters, this ratio is helpful for diagnosing flow rate problems of the samplers.

Figure 3 shows the scatter plots of SO_4^{2-} versus total S concentrations for each of the six sites. A good correlation ($R^2 = 0.98$) were observed for all the sites with a slope of 3.04±0.025 and an intercept of -0.477±0.093. The average sulfate to total sulfur ratio was determined to be 2.80±0.27, which meets the validation criteria (SO_4^{2-}/total S < 3.0).

Good correlations ($R^2 = 0.97 - 0.99$) were found for sulfate/total sulfur in $PM_{2.5}$ samples collected in individual sites. The regression statistics suggest a slope ranging from 2.97±0.058 to 3.11±0.072 and the intercepts are all at relatively low levels. The average sulfate/sulfur ratio ranges from 2.75±0.261 to 2.85±0.223. Both of the calculations indicate that most of the sulfur was present as soluble sulfate in $PM_{2.5}$.

Limits for outliers as suggested by USEPA [2012] are as follows,

Lower Limit: $[S]/[SO_4^{2-}] < 0.25$

Upper Limit: $[S]/[SO_4^{2-}] > 0.45$

The samples that are flagged as outliers with the corresponding $[S]/[SO_4^{2-}]$ ratios were listed in Table 11. It is noted that 3 out of 4 flagged samples are upper outliers, i.e. not all of the sulfur is present as SO_4^{2-}. The discrepancy could be explained by the existence of other S-containing compounds in $PM_{2.5}$, e.g. organosulfates.

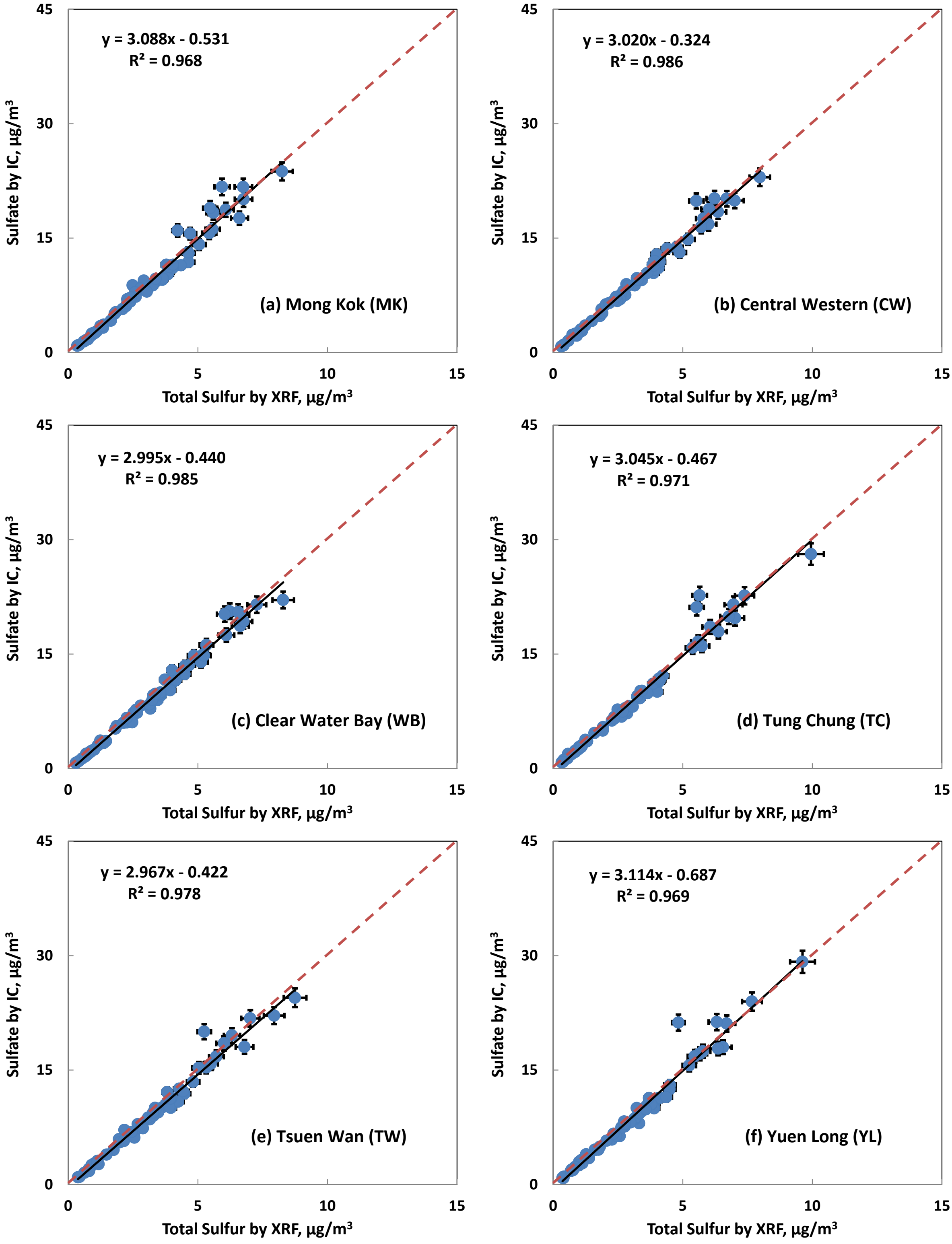


Figure 3. Scatter plots of sulfate versus total sulfur measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 10. Statistics analysis of sulfate versus total sulfur measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Slope	3.09 (±0.073)	3.02 (±0.047)	3.00 (±0.047)	3.05 (±0.068)	2.97 (±0.058)	3.11 (±0.072)	3.04 (±0.025)
Intercept	-0.531 (±0.265)	-0.324 (±0.173)	-0.440 (±0.180)	-0.467 (±0.257)	-0.422 (±0.213)	-0.687 (±0.265)	-0.477 (±0.093)
R^2	0.968	0.986	0.985	0.971	0.978	0.969	0.975
AVG total S	3.13	3.11	3.23	3.14	3.14	3.10	3.14
AVG SO_4^{2-}	9.14	9.08	9.25	9.08	8.88	8.96	9.07
AVG SO_4^{2-}/S	2.82 (±0.316)	2.85 (±0.223)	2.77 (±0.239)	2.81 (±0.284)	2.75 (±0.261)	2.79 (±0.308)	2.80 (±0.274)

Table 11. List of flagged samples from the [S]/[SO_4^{2-}] test.

Sample ID	[S]/[SO_4^{2-}] Ratio
TC130903	0.46
TW131217	0.46
YL130717	0.49
YL131226	0.23

3.3.2.2 Water-soluble Potassium (K^+) versus Total Potassium (K)

Water-soluble potassium (K^+) is measured by ion chromatography (IC) on QMA filters and the total potassium (K) is measured by X-Ray Fluorescence (XRF) on Teflon filters. The ratio of K^+ to K is expected to equal or be less than 1. Figure 4 shows the scatter plots of K^+ versus total K concentrations for each of the six sites. A good correlation ($R^2 = 0.94$) were observed for all the sites with a slope of 0.97±0.01 and an intercept of -0.04 ± 0.01. The ratio of water-soluble potassium to total potassium averages at 0.87±0.38, which meets the validation criteria (K^+/total K < 1).

Good correlations ($R^2 = 0.93 - 0.96$) were found for K^+/K in $PM_{2.5}$ samples collected in individual sites. The regression statistics suggest a slope ranging from 0.95±0.03 to 1.00±0.03 and the intercepts are all at relatively low levels.

Generally, almost all of the total potassium is in its soluble ionic form and a few scattered data points might be caused by instrumental and method uncertainties.

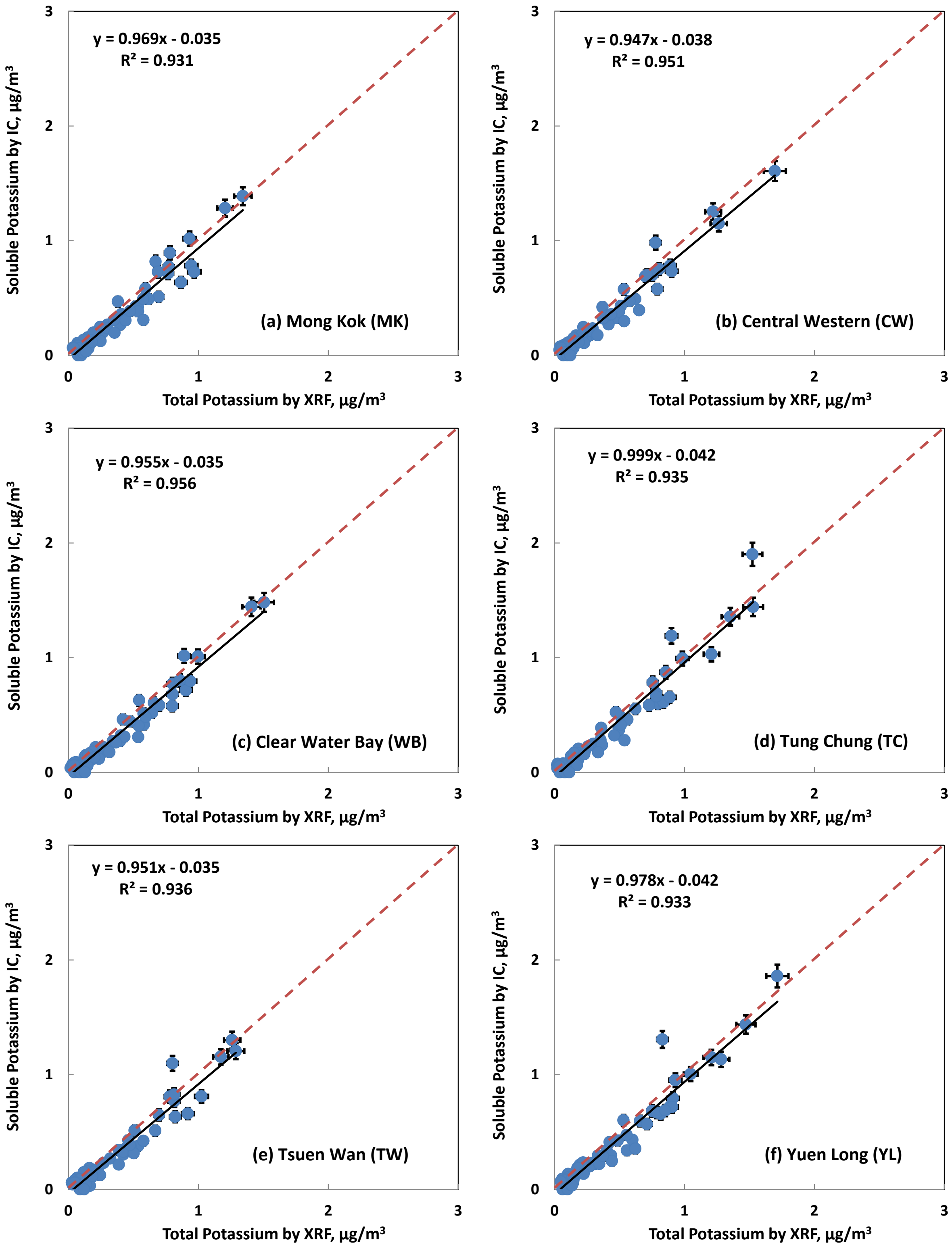


Figure 4. Scatter plots of water-soluble potassium versus total potassium measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 12. Statistics analysis of water-soluble potassium versus total potassium measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Slope	0.969 (±0.034)	0.947 (±0.028)	0.955 (±0.026)	0.999 (±0.034)	0.951 (±0.032)	0.978 (±0.034)	0.969 (±0.013)
Intercept	-0.035 (±0.016)	-0.038 (±0.014)	-0.035 (±0.013)	-0.042 (±0.019)	-0.035 (±0.016)	-0.042 (±0.020)	-0.038 (±0.007)
R^2	0.931	0.951	0.956	0.935	0.936	0.933	0.940
AVG total K	0.366	0.371	0.369	0.393	0.362	0.437	0.383
AVG K^+	0.319	0.314	0.318	0.350	0.309	0.385	0.333
AVG K^+/K	0.868 (±0.331)	0.817 (±0.314)	0.887 (±0.423)	0.937 (±0.524)	0.866 (±0.369)	0.861 (±0.297)	0.873 (±0.383)

3.3.2.3 Ammonium Balance

To further validate the ion measurements, calculated versus measured ammonium (NH_4^+) are compared. NH_4^+ is directly measured by IC analysis of QMA filter extract. NH_4^+ is very often found in the chemical forms of NH_4NO_3, $(NH_4)_2SO_4$, and NH_4HSO_4 while NH_4Cl is usually negligible and excluded from the calculation. Assuming full neutralization, measured NH_4^+ can be compared with the computed NH_4^+, which can be calculated in the following two ways,

Calculated NH_4^+ based on NH_4NO_3 and $(NH_4)_2SO_4 = 0.29 \times [NO_3^-] + 0.38 \times [SO_4^{2-}]$

Calculated NH_4^+ based on NH_4NO_3 and $NH_4HSO_4 = 0.29 \times [NO_3^-] + 0.192 \times [SO_4^{2-}]$

The calculated NH_4^+ is plotted against measured NH_4^+ for each of the six sites in Figure 5. For both forms of sulfate the comparisons show strong correlations ($R^2 = 0.99$ for ammonium sulfate and $R^2 = 0.97$ for ammonium bisulfate, respectively) but with quite different slopes. The slopes for individual sampling sites range from 1.04±0.02 at CW to 1.07±0.01 at WB assuming ammonium sulfate, and from 0.57±0.01 at WB to 0.64±0.02 at YL assuming ammonium bisulfate. These values were close to those found in earlier years. The average ratios of calculated ammonium to measured ammonium suggest that ammonium sulfate is the dominant form for sulfate in the $PM_{2.5}$ over the Hong Kong region in the year of 2013.

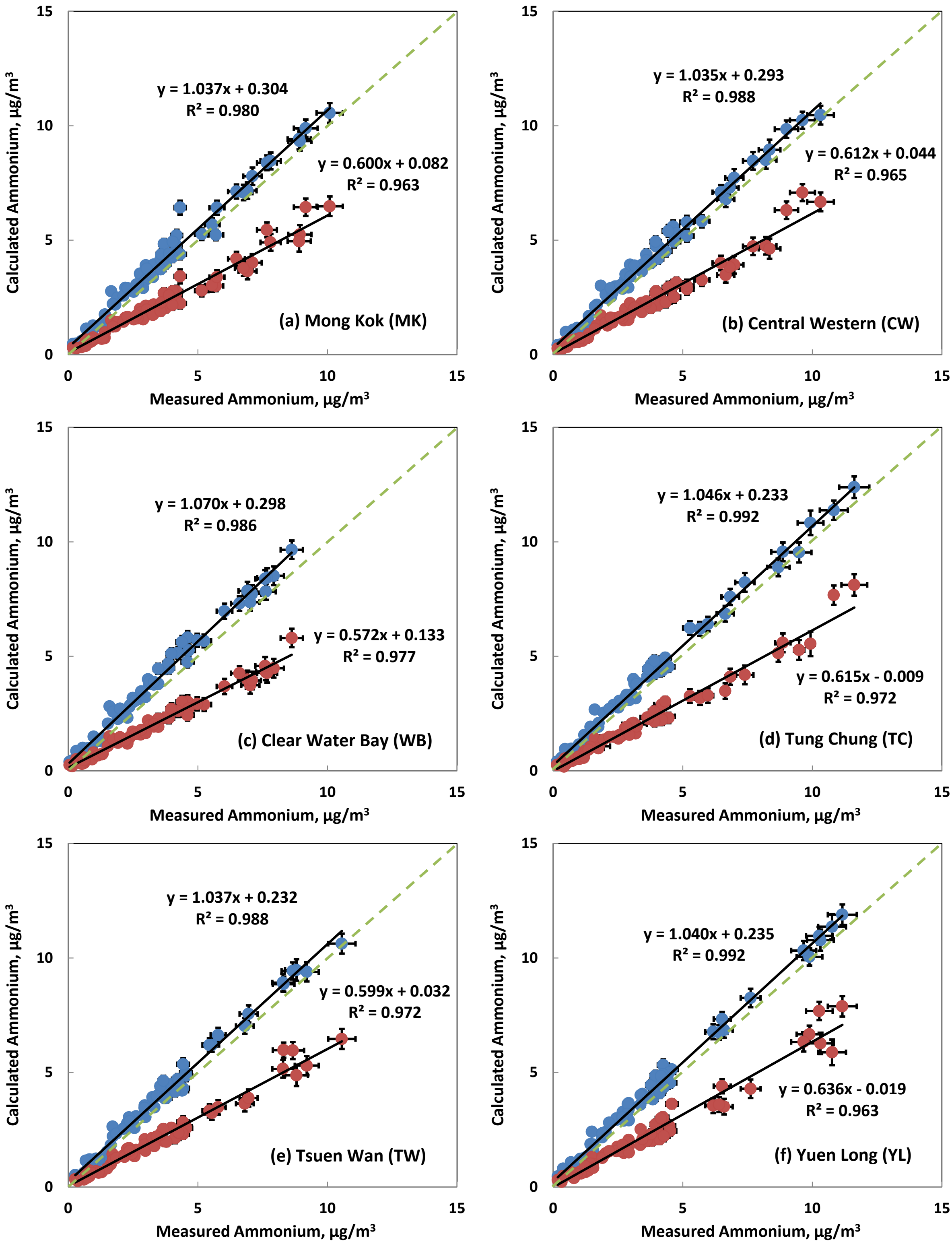


Figure 5. Scatter plots of calculated ammonium versus measured ammonium for PM$_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL. The calculated ammonium data are obtained assuming all nitrate was in the form of ammonium nitrate and all sulfate was in the form of either ammonium sulfate (data in blue) or ammonium bisulfate (data in brown).

Table 13. Statistics analysis of calculated ammonium versus measured ammonium for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Ammonium Sulfate (blue dots)							
Slope	1.04 (±0.019)	1.04 (±0.015)	1.07 (±0.016)	1.05 (±0.012)	1.04 (±0.015)	1.04 (±0.012)	1.04 (±0.006)
Intercept	0.304 (±0.081)	0.293 (±0.062)	0.298 (±0.064)	0.223 (±0.054)	0.232 (±0.060)	0.235 (±0.060)	0.270 (±0.026)
R^2	0.980	0.988	0.986	0.992	0.988	0.992	0.988
AVG Mea. NH_4^+	3.42	3.45	3.16	3.40	3.36	3.54	3.39
AVG Cal. NH_4^+	3.85	3.86	3.68	3.79	3.72	3.92	3.80
AVG Cal./Mea. NH_4^+	1.19 (±231)	1.19 (±0.223)	1.36 (±0.836)	1.18 (±0.259)	1.15 (±0.169)	1.17 (±0.247)	1.21 (±0.404)
Ammonium Bisulfate (brown dots)							
Slope	0.600 (±0.015)	0.612 (±0.015)	0.572 (±0.011)	0.615 (±0.013)	0.599 (±0.013)	0.636 (±0.016)	0.609 (±0.006)
Intercept	0.082 (±0.064)	0.044 (±0.065)	0.133 (±0.044)	-0.009 (±0.059)	0.032 (±0.054)	-0.019 (±0.072)	0.036 (±0.025)
R^2	0.963	0.965	0.977	0.972	0.972	0.963	0.967
AVG Mea. NH_4^+	3.42	3.45	3.16	3.40	3.36	3.54	3.39
AVG Cal. NH_4^+	2.14	2.15	1.94	2.08	2.05	2.23	2.10
AVG Cal./Mea. NH_4^+	0.665 (±0.164)	0.663 (±0.155)	0.741 (±0.558)	0.645 (±0.174)	0.633 (±0.118)	0.661 (±0.176)	0.668 (±0.271)

3.3.3 Charge Balance

For the anion and cation balance, the sum of Cl^-, NO_3^-, and SO_4^{2-} is compared to the sum of NH_4^+, Na^+, and K^+ in $\mu eq/m^3$ using the following equations:

$$\mu eq/m^3 \text{ for anions } = \left(\frac{Cl^-}{35.453} + \frac{NO_3^-}{62.005} + \frac{SO_4^{2-}}{96/2} \right)$$

$$\mu eq/m^3 \text{ for cations } = \left(\frac{NH_4^+}{18.04} + \frac{Na^+}{23.0} + \frac{K^+}{39.098} \right)$$

The cation equivalents are plotted against the anion equivalents in Figure 6. A strong correlation ($R^2 = 1.00$) was observed for the $PM_{2.5}$ samples collected at all of the sampling sites. Seen from the figure, the slopes obtained from individual sites range from 0.97 to 0.99 while the average Σanion/Σcation ratios range from 0.98±0.07 to 1.00±0.08.

The limits used for identifying outliers suggested by USEPA [2012] are as follows,

Lower Limit: [Sum of Anions]/[Sum of Cations] < 0.86

Upper Limit: [Sum of Anions]/[Sum of Cations] > 2.82

The samples that are identified as outliers according to these criteria are listed in Table 15. Compared to the [S]/[SO_4^{2-}] test, the charge balance is generally less useful for diagnosing specific problems of the samples since anions and cations are both captured on the same QMA filter. The [Anion]/[Cation] ratios were only taken as reference and the samples listed in Table 15 will not be flagged in this study because (1) only three anions and three cations were included in this balance test and any “missing” ions can upset the balance and (2) losses of volatile species (e.g. nitrate, chloride) during and after sampling are well documented [USEPA, 1999; Witz et al., 1990] and could lead to underestimation of these species.

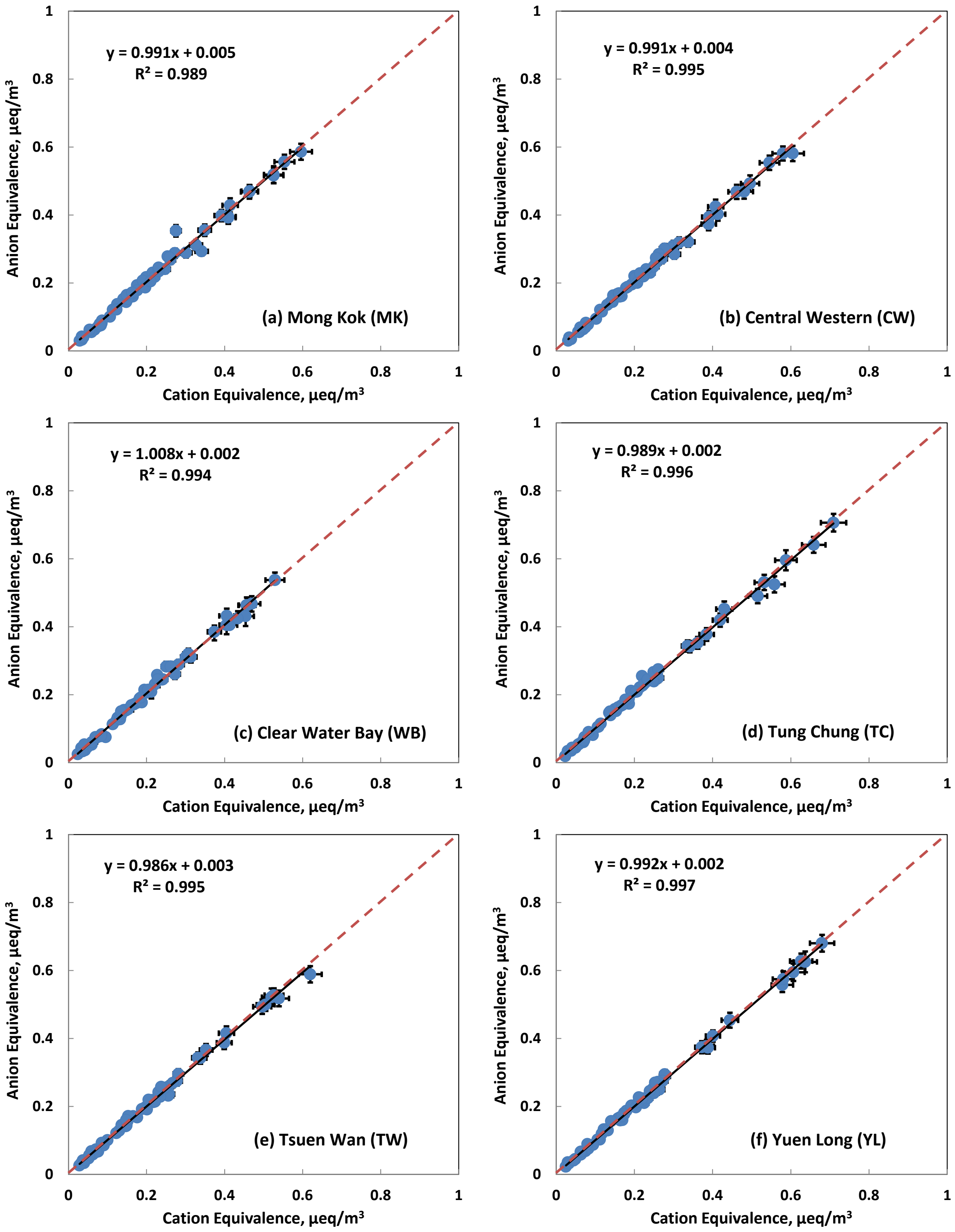


Figure 6. Scatter plots of anion versus cation measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 14. Statistics analysis of anion versus cation measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Slope	0.974 (±0.013)	0.975 (±0.009)	1.008 (±0.010)	0.989 (±0.008)	0.969 (±0.008)	0.976 (±0.007)	0.992 (±0.007)
Intercept	0.005 (±0.003)	0.003 (±0.002)	0.002 (±0.002)	0.002 (±0.002)	0.003 (±0.002)	0.001 (±0.002)	0.002 (±0.002)
R^2	0.989	0.995	0.994	0.996	0.995	0.997	0.997
AVG Σcation	0.212	0.214	0.201	0.210	0.207	0.218	0.218
AVG Σanion	0.211	0.212	0.205	0.211	0.203	0.214	0.218
AVG Σanion/Σcation	1.000 (±0.072)	0.993 (±0.057)	1.020 (±0.081)	0.995 (±0.066)	0.980 (±0.059)	0.980 (±0.058)	0.998 (±0.058)

Table 15. List of samples that were identified as outliers from the charge balance test.

Sample ID	$PM_{2.5}$ Mass (Teflon), μg/m^3	[Anion]/[Cation] Ratio
WB130518	11.71	0.79
WB130611	7.83	0.85
TC130903	6.56	0.81
TW130611	10.62	0.83

3.3.4 NIOSH_TOT versus IMPROVE_TOR for Carbon Measurements

Carbon concentrations were determined for the collected $PM_{2.5}$ samples by both NIOSH_TOT and IMPROVE_TOR methods. The total carbon concentrations obtained from NIOSH_TOT and IMPROVE_TOR reach an excellent agreement (Figure 7), giving credence to the validities of the analysis results from both methods. The comparison results of OC and EC determined by both methods for individual sites are shown in Figure 8. Generally, EC concentrations derived by NIOSH_TOT method were much lower than those by IMPROVE_TOR method. The difference in EC obtained by these two protocols has been well-documented and is primarily a result of protocol-dependent nature of correction of charring of OC formed during thermal analysis [e.g., Chow et al.,2004; Chen et al., 2004; Subraminan et al., 2006]. Seen from the results, the average ratios of NIOSH_TOT EC to IMPROVE_TOR EC for samples from individual sampling sites range from 0.32±0.13 at WB to 0.58±0.18 at MK (Table 16). No correlation was found between NIOSH_TOT EC and IMPROVE_TOR EC for samples collected at Mong Kok site, which have very high EC loading on the QMA filters.

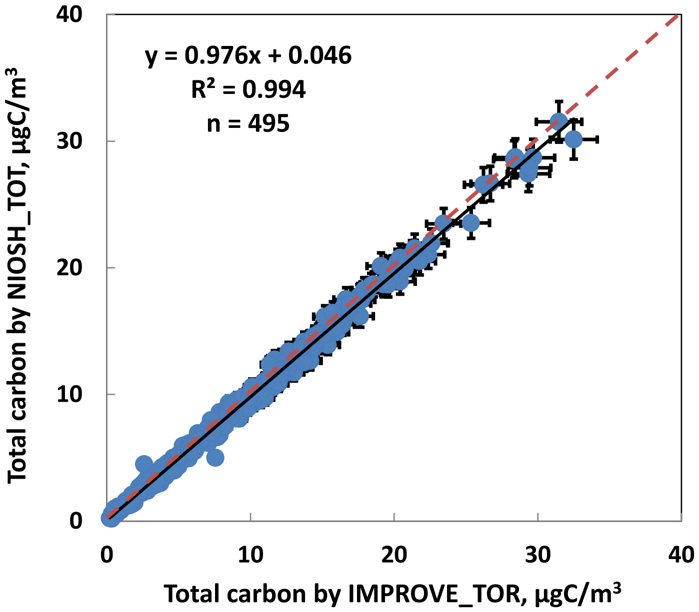
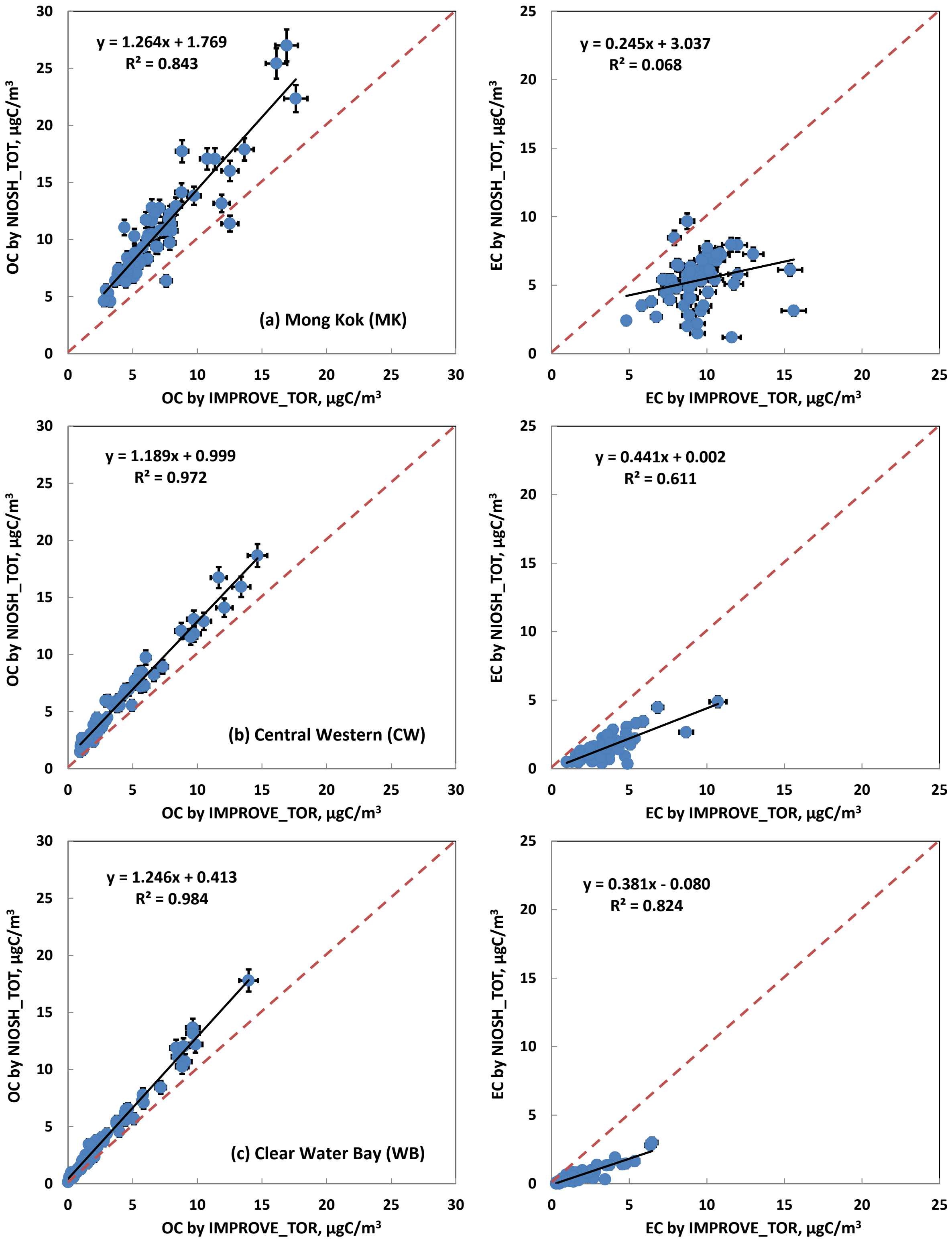


Figure 7. Comparisons of total carbon determined by NIOSH_TOT and IMPROVE_TOR methods for $PM_{2.5}$ samples collected at all sites.


y = 1.264x + 1.769
R² = 0.843
(a) Mong Kok (MK)
OC by NIOSH_TOT, μgC/m³
OC by IMPROVE_TOR, μgC/m³
0
5
10
15
20
25
30
y = 0.245x + 3.037
R² = 0.068
EC by NIOSH_TOT, μgC/m³
EC by IMPROVE_TOR, μgC/m³
0
5
10
15
20
25
y = 1.189x + 0.999
R² = 0.972
(b) Central Western (CW)
OC by NIOSH_TOT, μgC/m³
OC by IMPROVE_TOR, μgC/m³
y = 0.441x + 0.002
R² = 0.611
EC by NIOSH_TOT, μgC/m³
EC by IMPROVE_TOR, μgC/m³
y = 1.246x + 0.413
R² = 0.984
(c) Clear Water Bay (WB)
OC by NIOSH_TOT, μgC/m³
OC by IMPROVE_TOR, μgC/m³
y = 0.381x - 0.080
R² = 0.824
EC by NIOSH_TOT, μgC/m³
EC by IMPROVE_TOR, μgC/m³

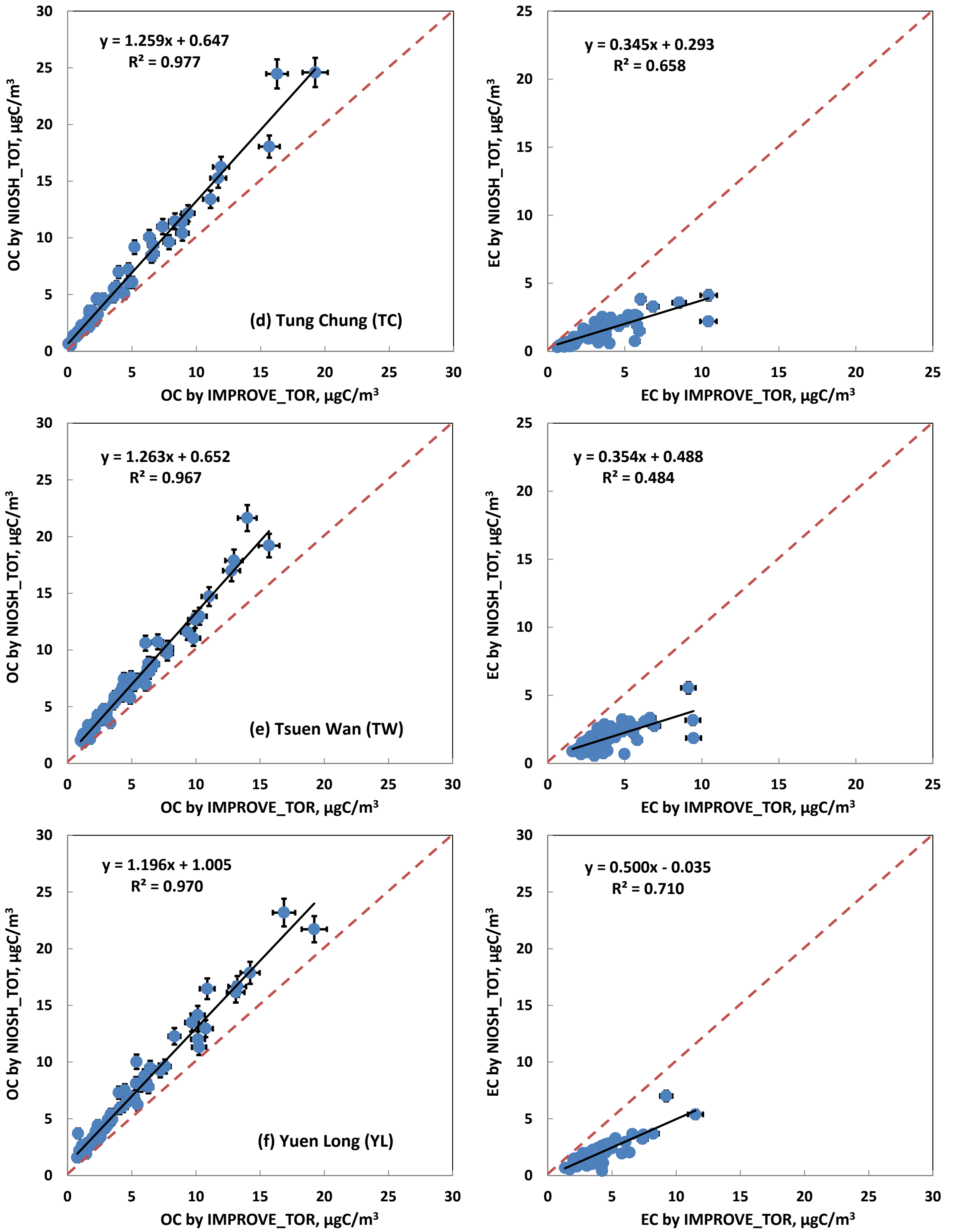


Figure 8. Comparisons of OC and EC determined by NIOSH_TOT and IMPROVE_TOR methods for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 16. Statistics analysis of OC and EC determined by NIOSH_TOT and IMPROVE_TOR methods for PM$_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
NIOSH_TOT OC versus IMPROVE_TOR OC							
Slope	1.26 (±0.070)	1.19 (±0.026)	1.25 (±0.020)	1.26 (±0.025)	1.26 (±0.030)	1.20 (±0.027)	1.27 (±0.015)
Intercept	1.77 (±0.540)	0.999 (±0.143)	0.413 (±0.093)	0.647 (±0.148)	0.652 (±0.179)	1.01 (±0.177)	0.758 (±0.094)
R^2	0.843	0.972	0.984	0.977	0.967	0.970	0.949
AVG TOR_OC	6.92	4.37	3.37	4.27	4.86	5.02	4.80
AVG TOT_OC	10.51	6.20	4.62	6.03	6.79	7.01	6.86
AVG TOT_OC/TOR_OC	1.57 (±0.267)	1.544 (±0.272)	1.60 (±0.719)	1.76 (±1.16)	1.487 (±0.241)	1.565 (±0.465)	1.59 (±0.620)
NIOSH_TOT EC versus IMPROVE_TOR EC							
Slope	0.245 (±0.117)	0.441 (±0.046)	0.381 (±0.023)	0.345 (±0.032)	0.354 (±0.047)	0.500 (±0.041)	0.539 (±0.017)
Intercept	3.037 (±1.127)	0.002 (±0.177)	-0.080 (±0.055)	0.293 (±0.128)	0.488 (±0.206)	-0.035 (±0.181)	-0.209 (±0.087)
R^2	0.068	0.611	0.824	0.658	0.484	0.710	0.742
AVG TOR_EC	9.42	3.48	1.96	3.37	4.01	3.96	4.37
AVG TOT_EC	5.35	1.54	0.67	1.46	1.91	1.95	2.15
AVG TOT_EC/TOR_EC	0.577 (±0.184)	0.444 (±0.157)	0.331 (±0.131)	0.452 (±0.133)	0.489 (±0.145)	0.495 (±0.143)	0.465 (±0.166)

3.3.5 Material Balance

Major PM components can be classified into seven categories including: 1) geological material, which can be estimated by (1.89 × [Al] + 2.14 × [Si] + 1.4 × [Ca] + 1.43 × [Fe]); 2) organic matter, which can be estimated from OC concentration as [OM] = 1.4 × [OC]; 3) soot which can be represented by EC concentration; 4) ammonium; 5) sulfate; 6) nitrate; 7) non-crustal trace elements; and 8) Unidentified material. Considering the large uncertainty in Na measurement by XRF, soluble sodium is used in calculation instead of total sodium. Therefore, the reconstructed mass is calculated by the following equation,

[Reconstructed Mass]

= 1.89 × [Al] + 2.14 × [Si] + 1.4 × [Ca] + 1.43 × [Fe]

+ 1.4 × [OC]

+ [EC]

+ $[NH_4^+]$

+ $[Na^+]$

+ [K]

+ $[SO_4^{2-}]$

+ $[NO_3^-]$

+ trace elements excluding Na, Al, Si, K, Ca, Fe, and S

The reconstructed mass is plotting against the measured mass in Figure 9. A strong correlation ($R^2 = 0.99$) is observed between the reconstructed mass and measured mass with a slope of 0.90±0.01. Different from the comparison made between sum of chemical species and measured mass (Figure 2), the major uncertainty of the reconstructed mass is due to the estimation of organic matter (OM). Generally, the concentration of OM is determined by multiplying the OC concentration by an empirical factor. In this study, a value of 1.4 was applied to this factor. It is worth noting that the [OM]/[OC] ratio is site dependent. The [OM]/[OC] ratio of freshly emitted aerosols is smaller than that of the more aging (oxygenated) aerosols. Since a constant conversion factor is adopted for calculation in this study, it can be seen that the average ratio of reconstructed mass to measured mass has the highest value for MK site, which is a roadside station and the dominant air mass is more freshly generated.

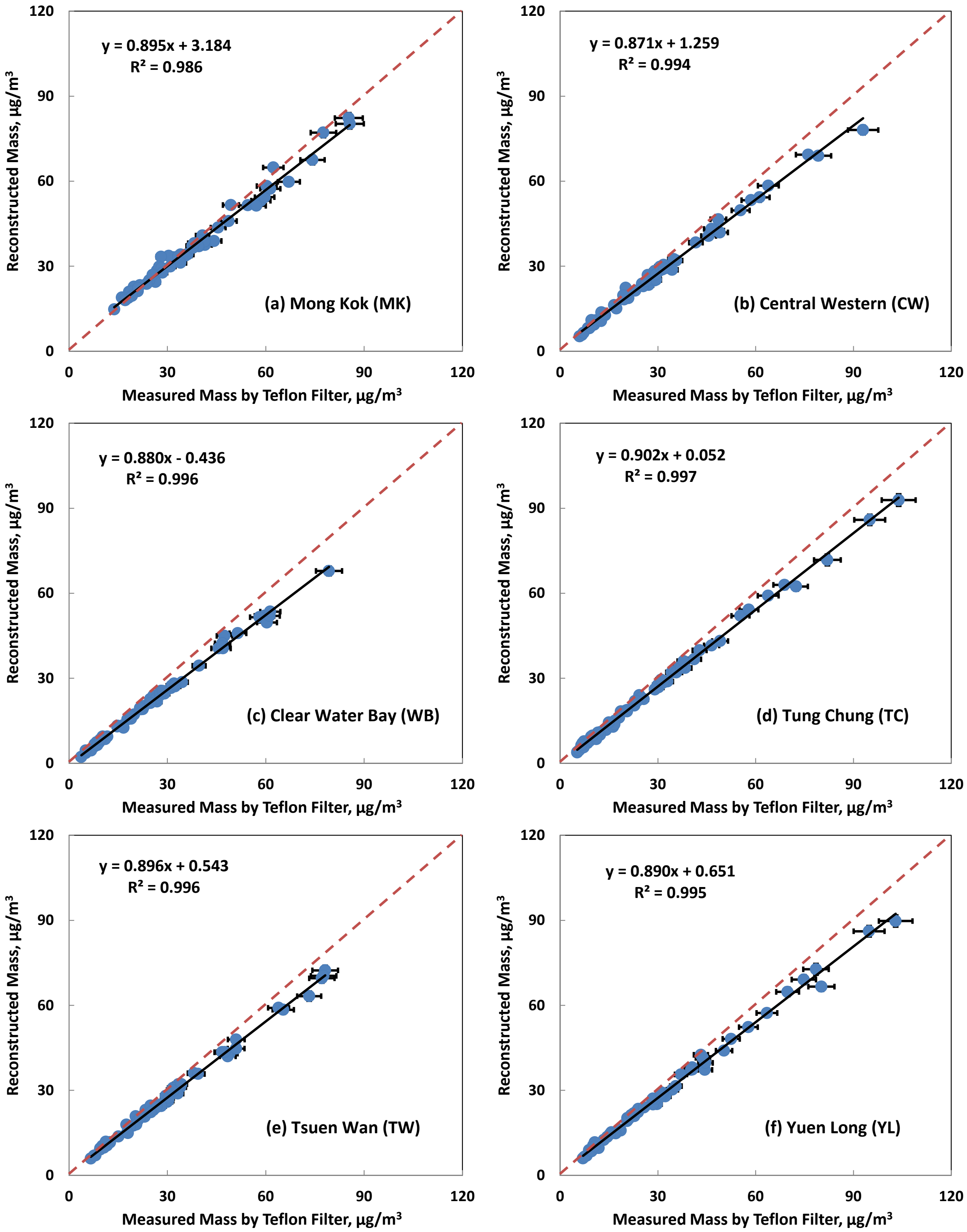


Figure 9. Scatter plots of reconstructed mass versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Table 17. Statistics analysis of reconstructed mass versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	ALL
n	62	61	62	62	62	62	371
Slope	0.895 (±0.014)	0.871 (±0.009)	0.880 (±0.007)	0.902 (±0.006)	0.896 (±0.008)	0.890 (±0.008)	0.900 (±0.005)
Intercept	3.184 (±0.569)	1.259 (±0.316)	-0.436 (±0.224)	0.052 (±0.220)	0.543 (±0.264)	0.651 (±0.305)	0.555 (±0.172)
R^2	0.986	0.994	0.996	0.997	0.996	0.995	0.990
AVG Mea. Mass	36.72	28.99	26.08	28.59	29.50	31.01	30.15
AVG Rec. Mass	36.06	26.50	22.51	25.84	26.98	28.27	27.70
AVG Rec./Mea. Mass	1.004 (±0.074)	0.927 (±0.059)	0.845 (±0.062)	0.897 (±0.063)	0.921 (±0.044)	0.918 (±0.049)	0.919 (±0.075)

The annual average composition (%) of the major components to the $PM_{2.5}$ mass is shown in Figure 10 for individual sites. The unidentified mass for MK, CW, WB, TC, TW, and YL is 0.8%, 7.3 %, 12.3%, 8.3%, 7.3%, and 7.5% of the measured mass, respectively. Overall, the reconstructed mass agrees with the measured mass within approx. 7%.

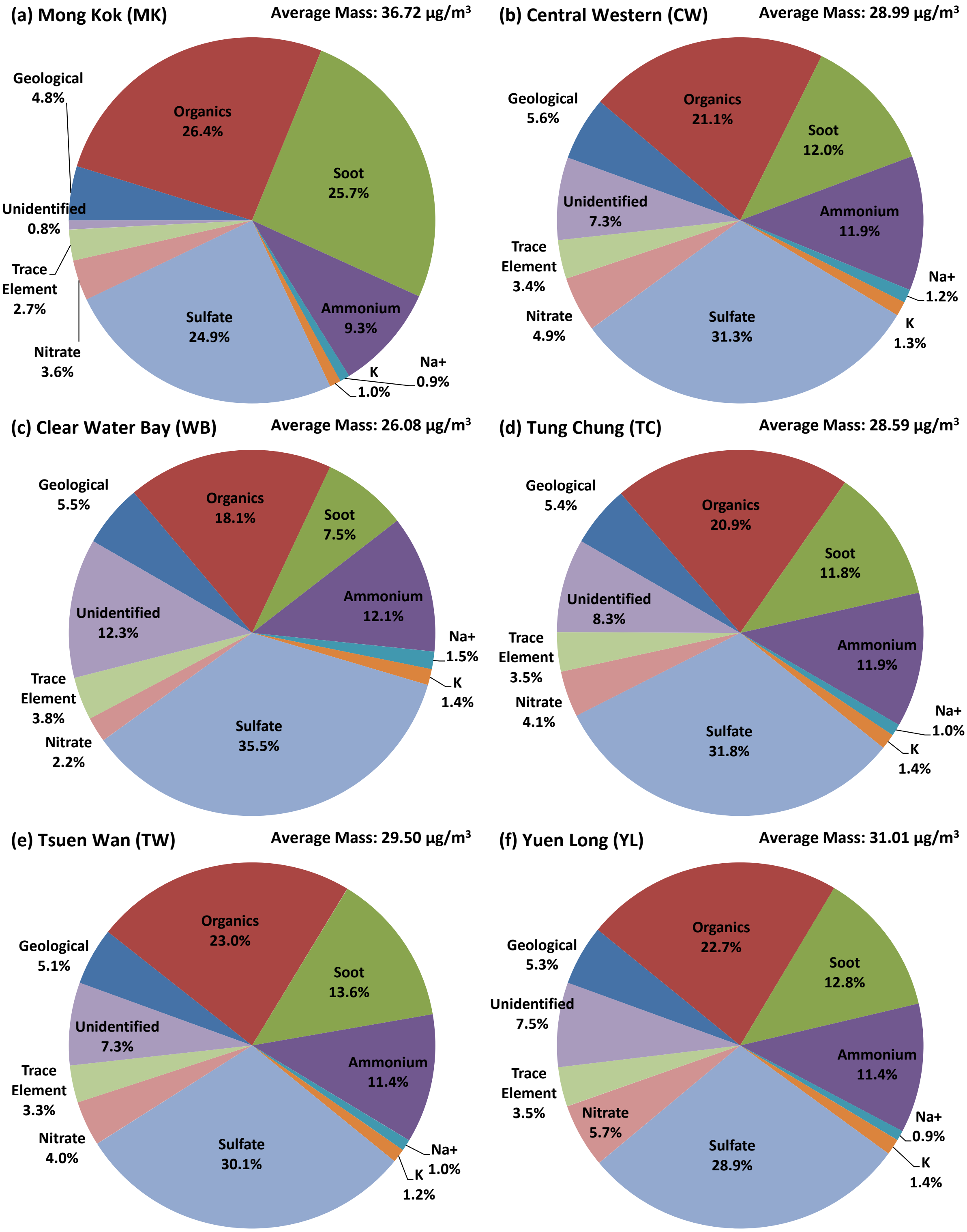


Figure 10. Annual average composition (%) of major components including 1) geological material; 2) organic matter; 3) soot; 4) ammonium; 5) sulfate; 6) nitrate; 7) non-crustal trace elements, and 8) Unidentified material (difference between measured mass and the reconstructed mass) to $PM_{2.5}$ mass for (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

Annually MK had the highest $PM_{2.5}$ loading while WB had the lowest (Figure 11). For all of the six sites, sulfate and OM were the two most abundant components followed by ammonium and soot (EC by IMPROVE_TOR method). The EC concentration was the highest at MK and the lowest at WB, which is consistent with the natures of the sampling sites. The concentrations of sulfate, ammonium, geological materials, and trace elements didn't vary much across all six sites.

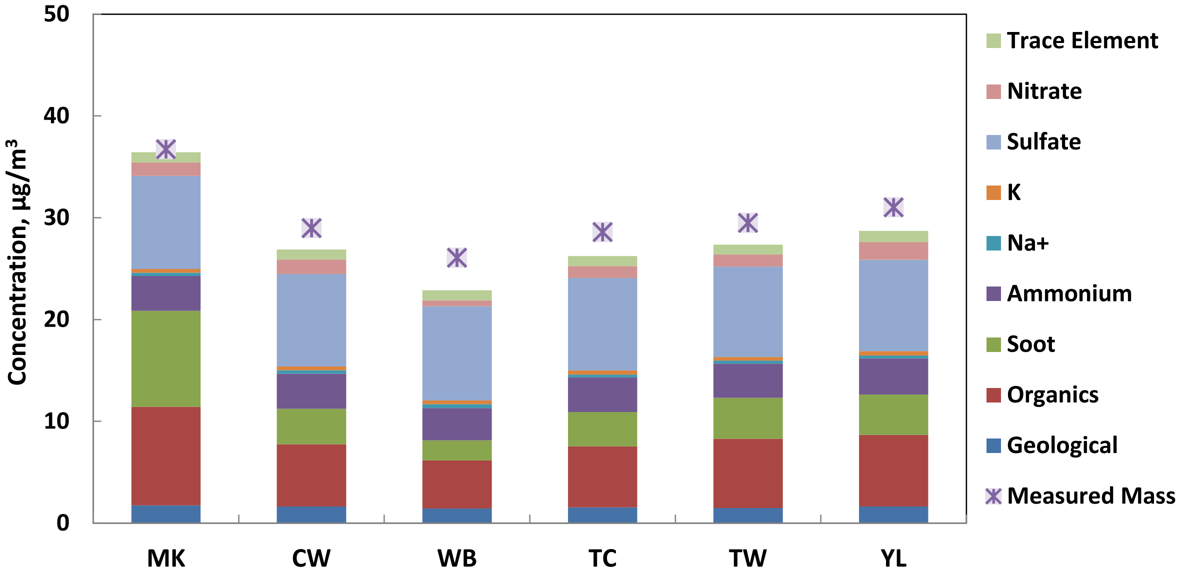


Figure 11. Comparison of annual average concentrations of major components including 1) geological material; 2) organic matter; 3) soot; 4) ammonium; 5) sulfate; 6) nitrate; 7) non-crustal trace elements, and 8) Unidentified material (difference between measured mass and the reconstructed mass) to $PM_{2.5}$ mass between individual sites.

3.3.6 Analysis of Collocated Data

The Hong Kong $PM_{2.5}$ speciation network operated four sites with collocated samplers during 2013, as shown in Table 2. The MK and CW sites included a third Partisol sampler for Teflon filters while the WB and TC sites included a third Partisol sampler for QMA filters. The collocated samplers run on a 1-in-6 day schedule as the primary samplers did. The data from the sites with collocated samplers affords an opportunity to calculate total precision and compare the values with the uncertainty values that are currently being reported to HKEPD.

The data used for comparison were subject to a data screening procedure including two steps. First, species that can be quantified (concentration > 2×LOD) more than 70% of the time will be included. Second, if either of the values in one pair of samples is below the LOQ, the whole pair of samples will be removed from the data set.

The Figures 12-21 show examples of the comparisons for $PM_{2.5}$ mass by gravimetric analysis, sulfur, potassium, and calcium by XRF, ammonium and sulfate by IC, OC and EC by NIOSH_TOT and IMPROVE_TOR. The least-squares linear regression parameters (slope, intercept, and R^2) by sites for each of these species are also included. These figures demonstrate good or excellent agreement for the major analytes.

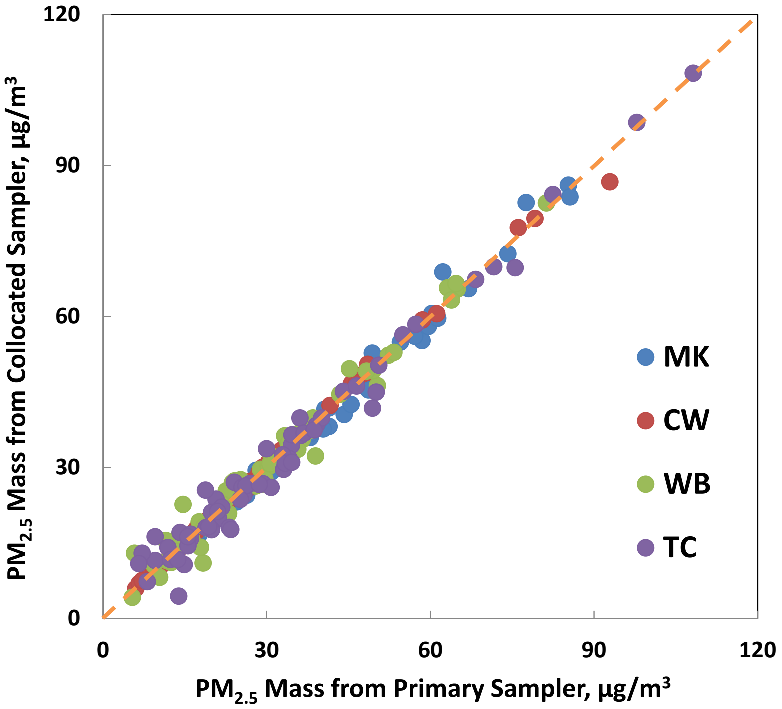


Figure 12. Collocated data for PM$_{2.5}$ mass concentration at MK, CW, WB and TC sites during 2013.

Table 18. Statistics analysis of collocated data for PM$_{2.5}$ mass concentration at MK, CW, WB and TC sites during 2013.

Statistics/Site	MK	CW	WB	TC
n	118	120	124	124
Slope	1.01 (±0.013)	0.988 (±0.007)	0.995 (±0.020)	0.978 (±0.019)
Intercept	-0.632 (±0.533)	0.571 (±0.222)	0.357 (±0.678)	0.192 (±0.717)
R^2	0.991	0.997	0.977	0.979

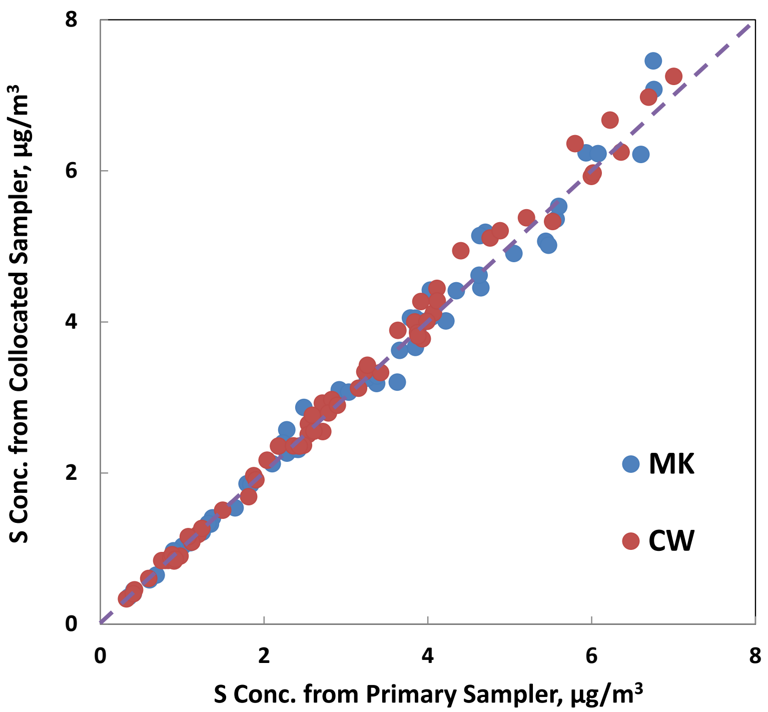


Figure 13. Collocated data for sulfur concentration at MK and CW sites during 2013.

Table 19. Statistics analysis of collocated data for sulfur concentration at MK and CW sites during 2013.

Statistics/Site	MK	CW
n	118	120
Slope	0.994 (±0.016)	1.03 (±0.011)
Intercept	0.040 (±0.059)	-0.022 (±0.038)
R^2	0.986	0.994

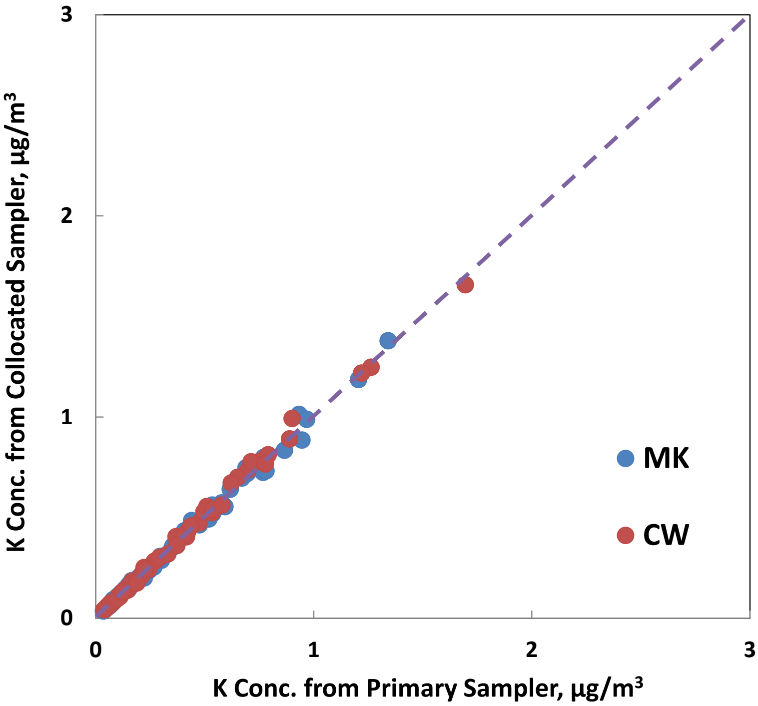


Figure 14. Collocated data for potassium concentration at MK and CW sites during 2013.

Table 20. Statistics analysis of collocated data for potassium concentration at MK and CW sites during 2013.

Statistics/Site	MK	CW
n	118	120
Slope	1.00 (±0.010)	1.01 (±0.008)
Intercept	0.001 (±0.005)	0.005 (±0.004)
R^2	0.995	0.996

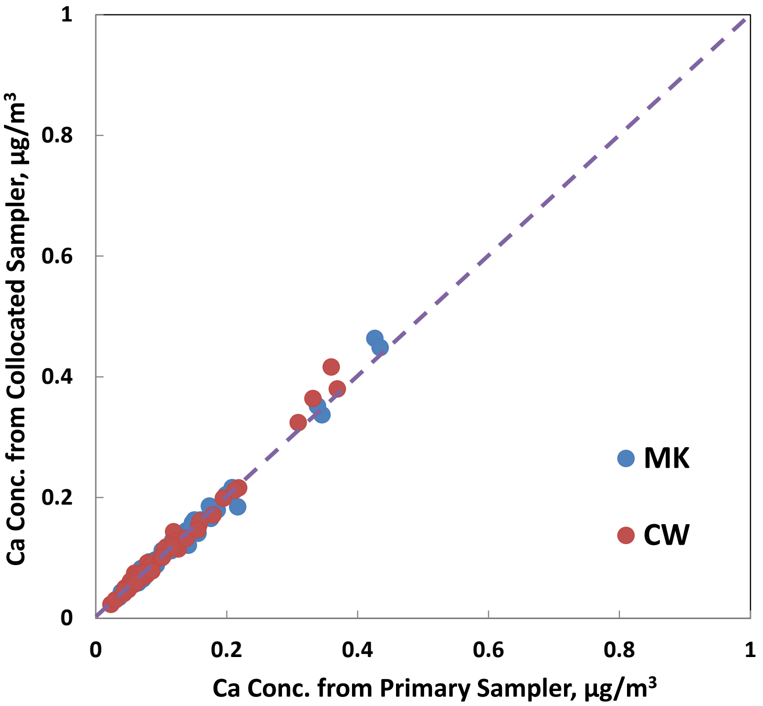


Figure 15. Collocated data for calcium concentration at MK and CW sites during 2013.

Table 21. Statistics analysis of collocated data for calcium concentration at MK and CW sites during 2013.

Statistics/Site	MK	CW
n	118	120
Slope	1.02 (±0.015)	1.06 (±0.015)
Intercept	-0.001 (±0.002)	-0.004 (±0.002)
R^2	0.989	0.988

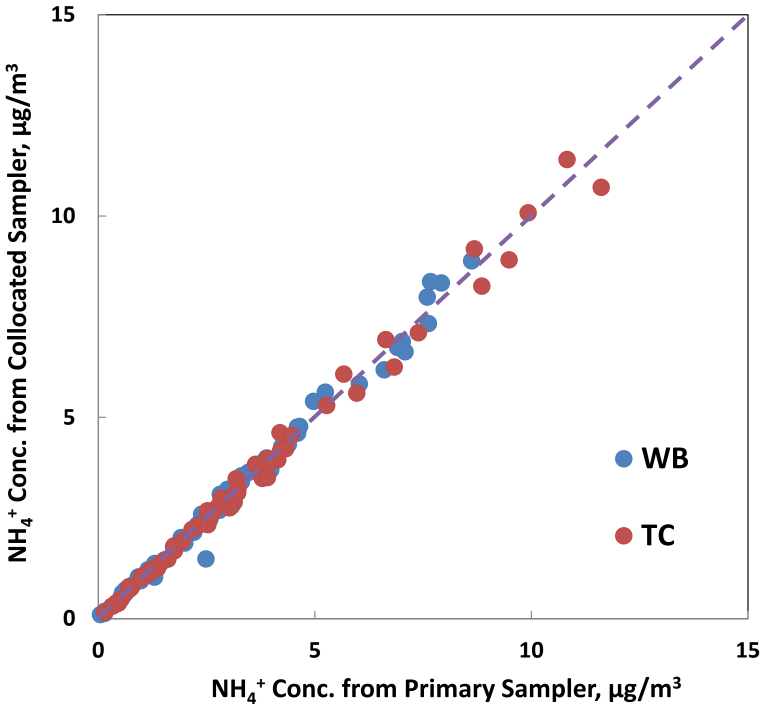


Figure 16. Collocated data for ammonium concentration at WB and TC sites during 2013.

Table 22. Statistics analysis of collocated data for ammonium concentration at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	1.01 (±0.013)	0.983 (±0.012)
Intercept	-0.029 (±0.052)	0.011 (±0.050)
R^2	0.989	0.992

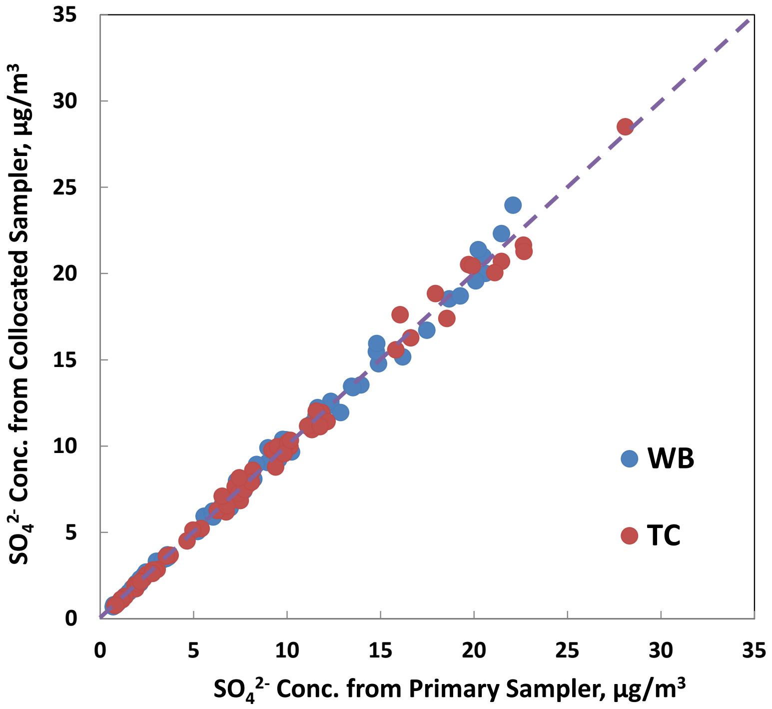


Figure 17. Collocated data for sulfate concentration at WB and TC sites during 2013.

Table 23. Statistics analysis of collocated data for sulfate concentration at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	1.01 (±0.010)	0.989 (±0.010)
Intercept	0.002 (±0.115)	0.017 (±0.110)
R^2	0.994	0.994

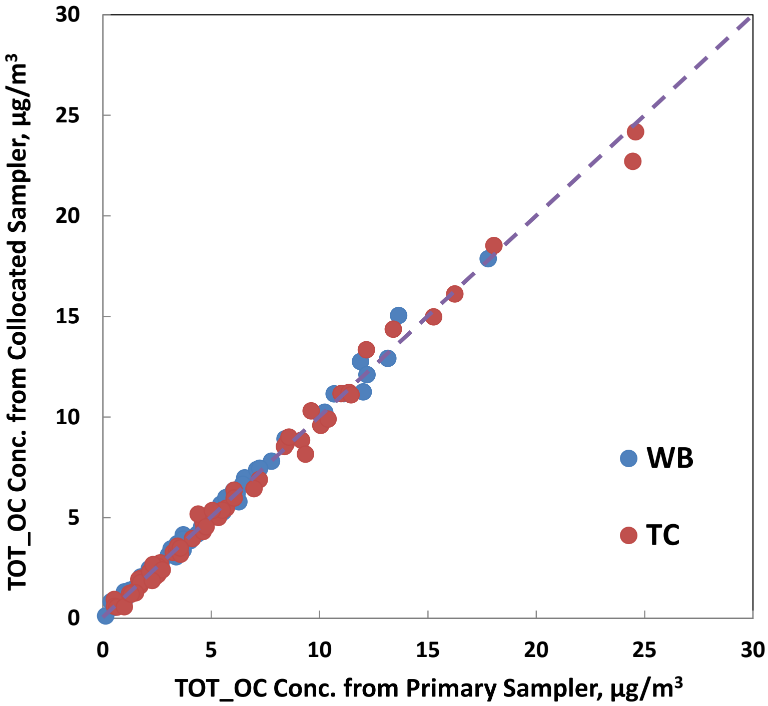


Figure 18. Collocated data for OC concentration by NIOSH_TOT method at WB and TC sites during 2013.

Table 24. Statistics analysis of collocated data for OC concentration by NIOSH_TOT method at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	1.02 (±0.010)	0.985 (±0.010)
Intercept	0.005 (±0.059)	0.012 (±0.083)
R^2	0.994	0.993

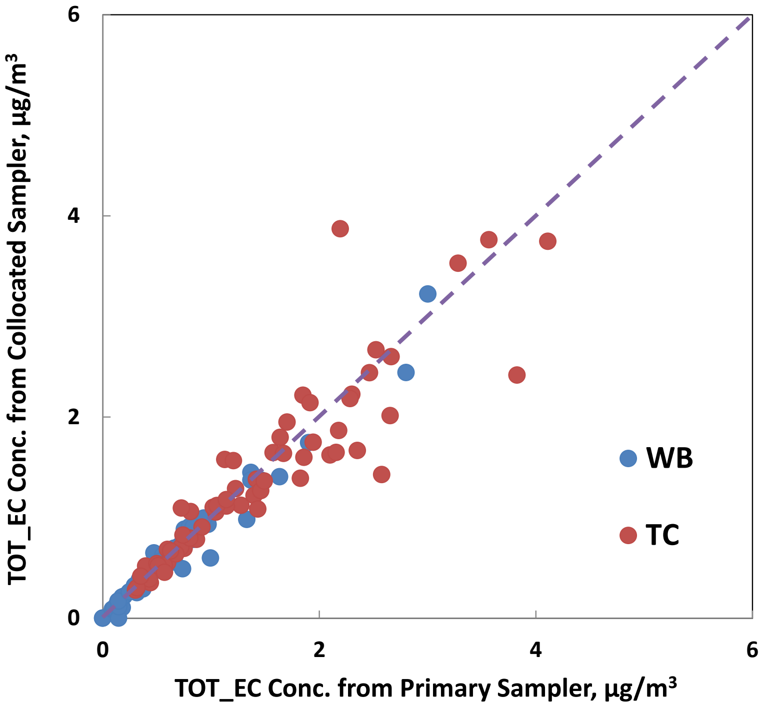


Figure 19. Collocated data for EC concentration by NIOSH_TOT method at WB and TC sites during 2013.

Table 25. Statistics analysis of collocated data for EC concentration by NIOSH_TOT method at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	0.953 (±0.024)	0.872 (±0.052)
Intercept	0.017 (±0.021)	0.138 (±0.090)
R^2	0.963	0.822

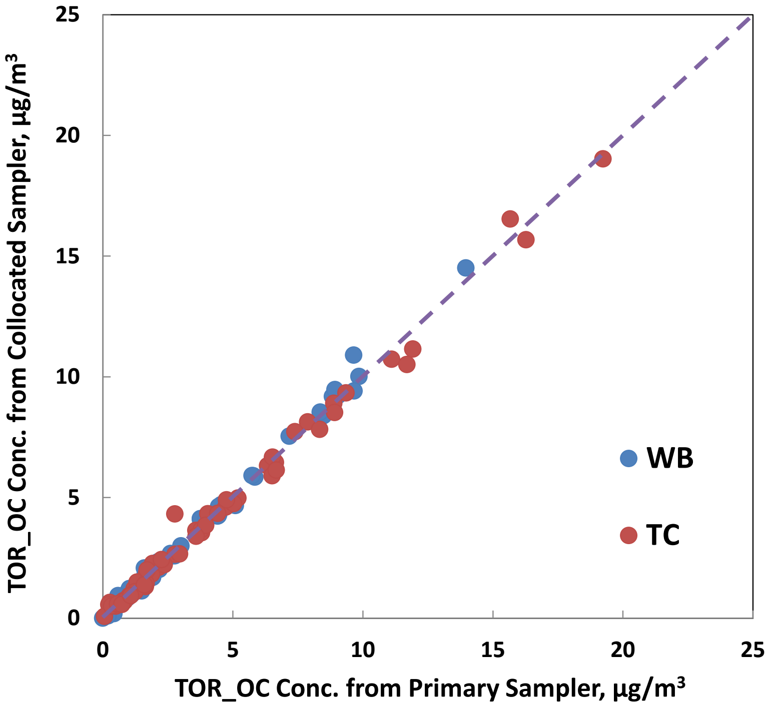


Figure 20. Collocated data for OC concentration by IMPROVE_TOR method at WB and TC sites during 2013.

Table 26. Statistics analysis of collocated data for OC concentration by IMPROVE_TOR method at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	1.03 (±0.010)	0.978 (±0.011)
Intercept	-0.054 (±0.044)	0.028 (±0.065)
R^2	0.995	0.993

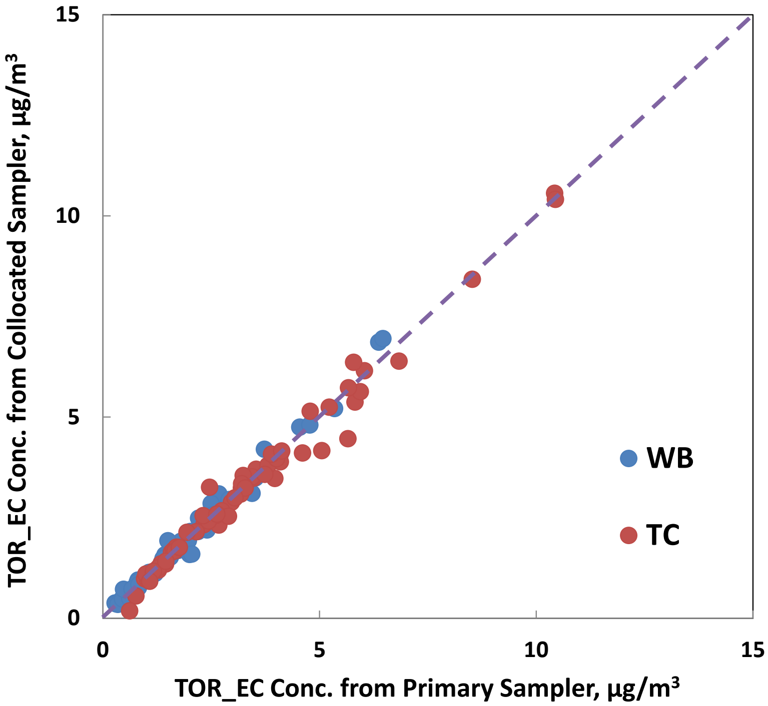


Figure 21. Collocated data for EC concentration by IMPROVE_TOR method at WB and TC sites during 2013.

Table 27. Statistics analysis of collocated data for EC concentration by IMPROVE_TOR method at WB and TC sites during 2013.

Statistics/Site	WB	TC
n	124	124
Slope	1.03 (±0.016)	0.984 (±0.017)
Intercept	-0.025 (±0.040)	-0.013 (±0.069)
R^2	0.985	0.982

Bias and precisions were computed for collocated comparisons on $PM_{2.5}$ mass and select chemical species with the screened data set. The equations used are as below,

$$\overline{C_i} = \frac{X_i + Y_i}{2} \tag{10}$$

$$\%RB_i = \frac{(Y_i - X_i)}{\overline{C_i}} \times 100\% \tag{11}$$

$$\%\overline{RB} = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_i - X_i) \times 100\%}{\overline{C_i}} \tag{12}$$

$$\%RSD = \frac{\left|\%RB_i\right|}{\sqrt{2}} \tag{13}$$

$$\%\overline{RSD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\%RSD_i^2} \tag{14}$$

Where:

X_i = ambient air concentration of sample i measured at sampler X, µg/m^3

Y_i = ambient air concentration of sample i measured at collocated sampler Y, µg/m^3

n = number of paired samples

%RB = percent relative bias

%RSD = percent relative standard deviation (precision)

The uncertainty values reported to HKEPD are summarized under the column titled “Avg. UNC” in Table 28. This is the average of all the relative uncertainties reported to HKEPD over the collocated data set and is calculated as follows,

$$\overline{UNC} = \frac{1}{n}\sum_{i}\sum_{j}\frac{UNC_{ij}}{CONC_{ij}} \tag{15}$$

Where:

$CONC_{ij}$ = concentration for the ith exposure with the jth sampler (j = 1 or 2), µg/m^3

UNC_{ij} = uncertainty for the ith exposure with the jth sampler (j = 1 or 2), µg/m^3

n = total number of measurements

The column titled “UNC/RSD” is essentially the average under- or over-estimate of the uncertainty for each chemical species reported during 2013. Ratios greater than 200% or less than 50% indicate situations in which the uncertainties reported HKEPD were different from the uncertainties estimated from collocated data by a factor of 2 or more. The column titled “Counts” shows the number of observations included in the averages subject to the criteria defined above.

Table 28. Average relative biases and average relative standard deviations (precisions) of concentrations of $PM_{2.5}$ mass and select chemical species for collocated samples.

	%RB	%RSD	Avg. UNC[1]	UNC/RSD[2]	Counts[3]
$PM_{2.5}$_Teflon	0.2%	2.4%	N/A	N/A	238
$PM_{2.5}$_QMA	7.2%	12.9%	N/A	N/A	248
Na^+	-1.6%	7.1%	22.4%	**317.0%**	246
NH_4^+	-0.6%	6.7%	5.8%	86.3%	248
K^+	0.5%	7.9%	28.0%	**357.0%**	232
Cl^-	-5.3%	15.1%	47.0%	**311.7%**	146
NO_3^-	0.2%	13.3%	31.8%	**239.1%**	220
SO_4^{2-}	-0.3%	3.4%	5.4%	161.8%	248
TOR_OC	1.7%	7.5%	10.8%	144.2%	216
TOR_EC	-1.6%	6.4%	8.9%	138.8%	248
TOT_OC	0.6%	7.4%	16.9%	**229.0%**	244
TOT_EC	1.9%	12.4%	57.9%	**465.5%**	242
Al	0.6%	4.3%	15.0%	**348.0%**	188
Si	-4.8%	8.7%	12.6%	144.4%	206
P	-1.9%	23.1%	27.0%	116.8%	202
S	1.6%	4.3%	5.1%	119.8%	238
K	1.2%	4.0%	5.4%	136.2%	238
Ca	0.4%	5.2%	8.4%	161.2%	238
Ti	-3.1%	11.5%	18.4%	160.6%	202
V	0.2%	7.2%	11.3%	156.6%	238
Fe	0.5%	5.4%	6.6%	122.3%	238
Ni	3.8%	7.2%	19.9%	**275.6%**	158
Cu	4.4%	9.6%	16.6%	173.6%	206
Zn	1.3%	5.4%	12.0%	**222.5%**	212
Br	1.1%	15.3%	15.5%	101.5%	160

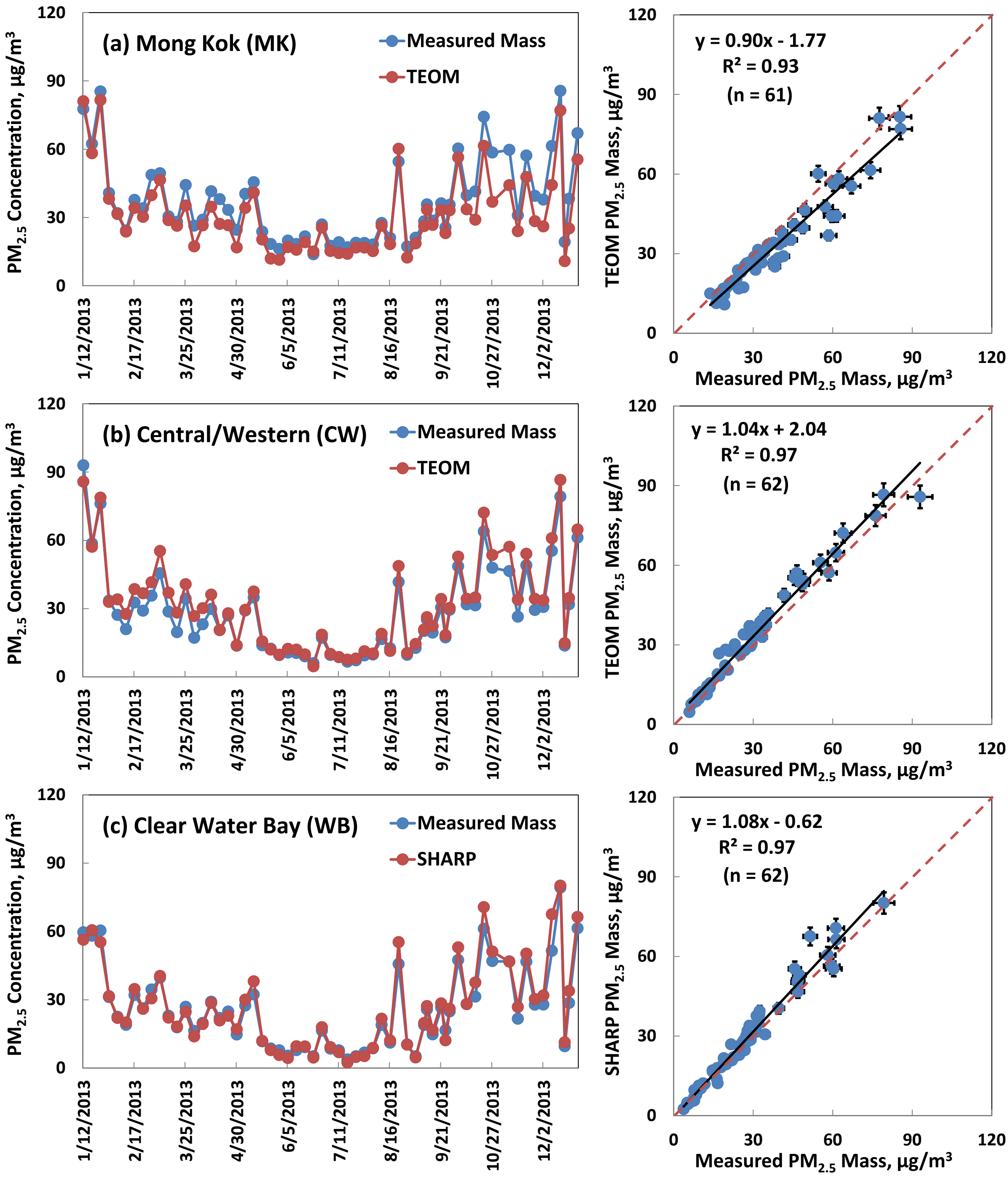
[1] Average value of the relative uncertainties as reported to HKEPD.

[2] UNC/RSD is the ratio of reported uncertainties divided by the uncertainty determined by collocated samples. Values greater than 200% or less than 50% are shown in bold.

[3] Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above the LOQ were included.

3.3.7 $PM_{2.5}$ Mass Concentrations: Gravimetric vs. Continuous Measurements

Continuous monitoring of $PM_{2.5}$ concentrations were also conducted at all six monitoring sites. TEOMs (Tapered Element Oscillating Microbalance) are installed at MK, CW, TC, and TW sites. At YL site, TEOM was running until mid-2013 and a Beta Attenuation Monitor (BAM-1020, Met One Instruments) was deployed for $PM_{2.5}$ monitoring since June 2013. At WB site, a Synchronized Hybrid Ambient Real-time Particulate Monitor (Model 5030 SHARP, Thermo Scientific) has been set up for continuous $PM_{2.5}$ monitoring since May 2011. Comparisons of $PM_{2.5}$ mass concentrations from gravimetric measurement and 24-hr average TEOM/beta gauge measurement were conducted. The results are presented in both time-series plots and scatter plots (Figure 22). Uncertainties of TEOM/beta gauge are assumed to be 5% of concentration. The two measurements show good agreement ($R^2 = 0.92 - 0.99$) with slopes ranging from 0.87 to 1.08.


(a) Mong Kok (MK)
Measured Mass
TEOM
(b) Central/Western (CW)
Measured Mass
TEOM
(c) Clear Water Bay (WB)
Measured Mass
SHARP
$PM_{2.5}$ Concentration, μg/m³
0
30
60
90
120
1/12/2013
2/17/2013
3/25/2013
4/30/2013
6/5/2013
7/11/2013
8/16/2013
9/21/2013
10/27/2013
12/2/2013
y = 0.90x - 1.77
R² = 0.93
(n = 61)
y = 1.04x + 2.04
R² = 0.97
(n = 62)
y = 1.08x - 0.62
R² = 0.97
(n = 62)
TEOM $PM_{2.5}$ Mass, μg/m³
SHARP $PM_{2.5}$ Mass, μg/m³
Measured $PM_{2.5}$ Mass, μg/m³

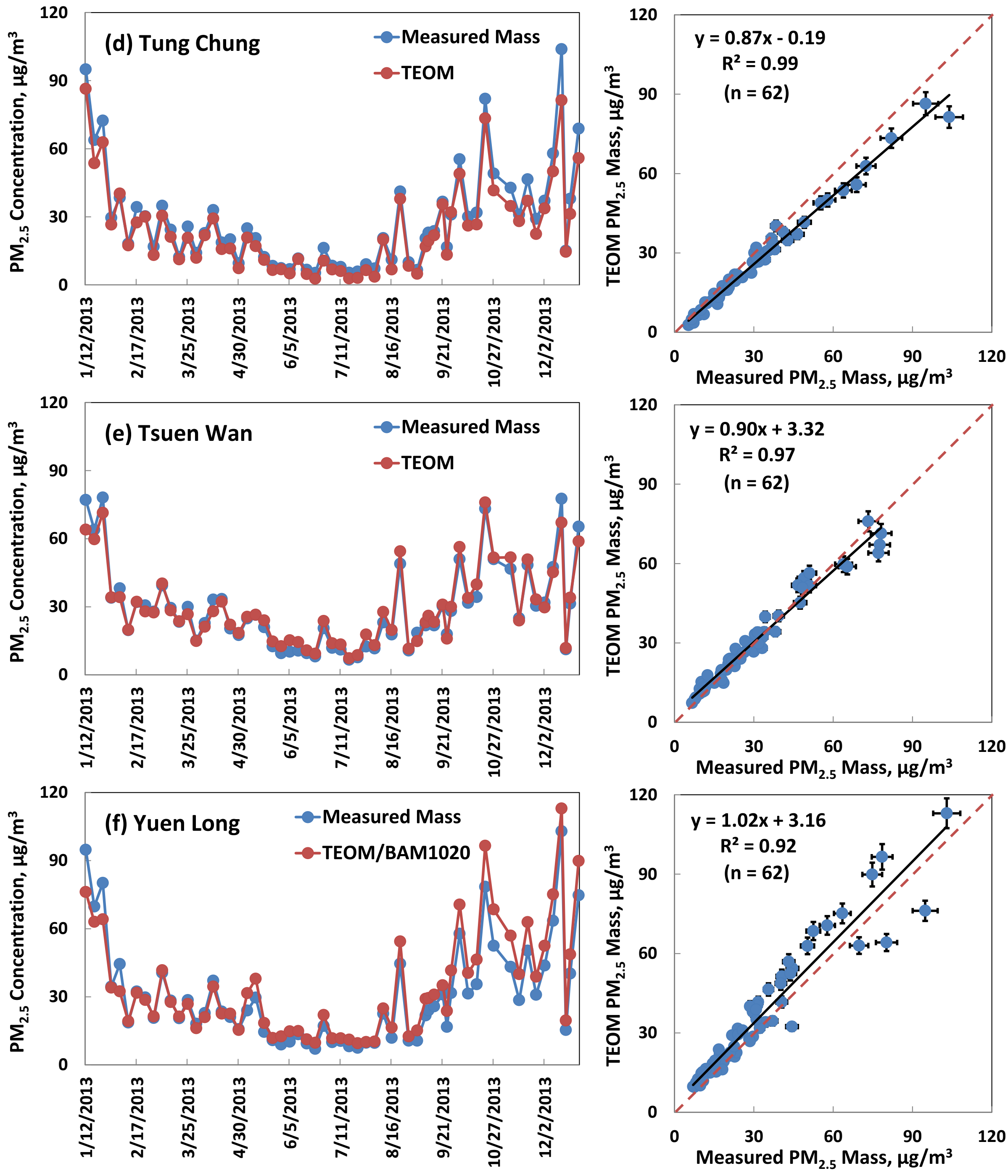


Figure 22. Comparisons of PM$_{2.5}$ mass concentrations from gravimetric and continuous measurements at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

4. Comparison to the $PM_{2.5}$ Sampling Campaigns in 2000-2001, 2004-2005, 2008-2009, 2011 and 2012

A side-by-side comparison of the six one-year studies of $PM_{2.5}$ samples collected during 2000-2001, 2004-2005, 2008-2009, the whole year of 2011, the whole year of 2012, the current 2013 period is shown in Appendix A [Chow et al., 2002, 2006, 2010; Yu et al., 2012, 2013]. In this study, the $PM_{2.5}$ monitoring sites remained the same as those in the years of 2011 and 2012.

Compared to the year of 2012, the annual average $PM_{2.5}$ concentrations at MK and YL sites in 2013 exhibited increases of 5.8% and 10.9%, respectively. On the other hand, decreases of 1.1%, 9.3%, 1.7%, and 5.6% were observed at CW, WB, TC, and TW sites, respectively. Annual trends of $PM_{2.5}$ mass were examined for MK, TW, and YL sites since these three sites have been in the monitoring network for a longer time. In general, the fine PM levels at all three sites have been decreasing since 2000.

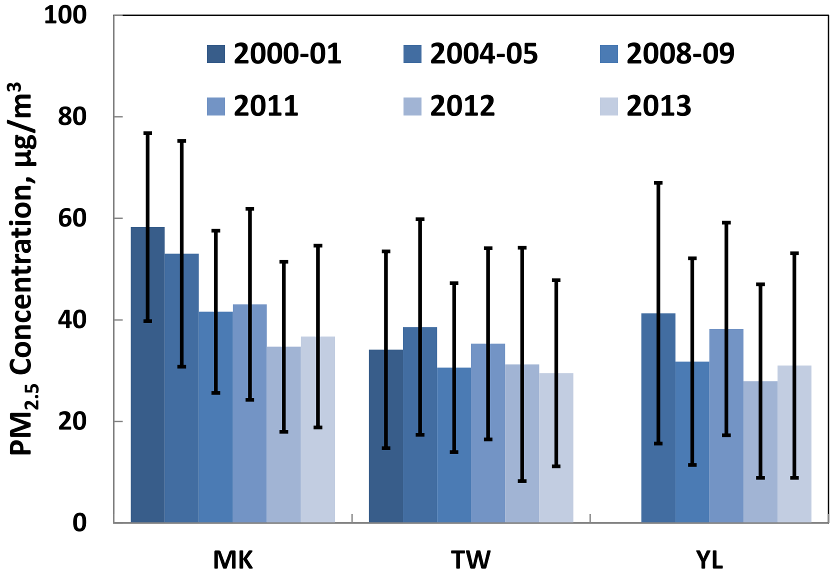


Figure 23. Comparisons of annual average $PM_{2.5}$ mass concentrations at MK, TW, and YL sites from 2000 to 2013. The error bars represent standard deviations which are a function of the natural variability of the environmental levels and are not indicative of the analytical precision.

Measured species were grouped into six categories described in Section 3.3.5 for better comparison (Figure 24). For OC, EC and sulfate, high concentration levels were observed in the first two studies (i.e. 2000-01 and 2004-05) and then the concentrations maintained at lower levels since 2008. For nitrate, the concentration level remained high till 2011 and then a notable decrease was observed since 2012. For other species (i.e., geological material, ammonium, sodium, potassium, and non-crustal elements), the concentrations were at similar levels all over the years.

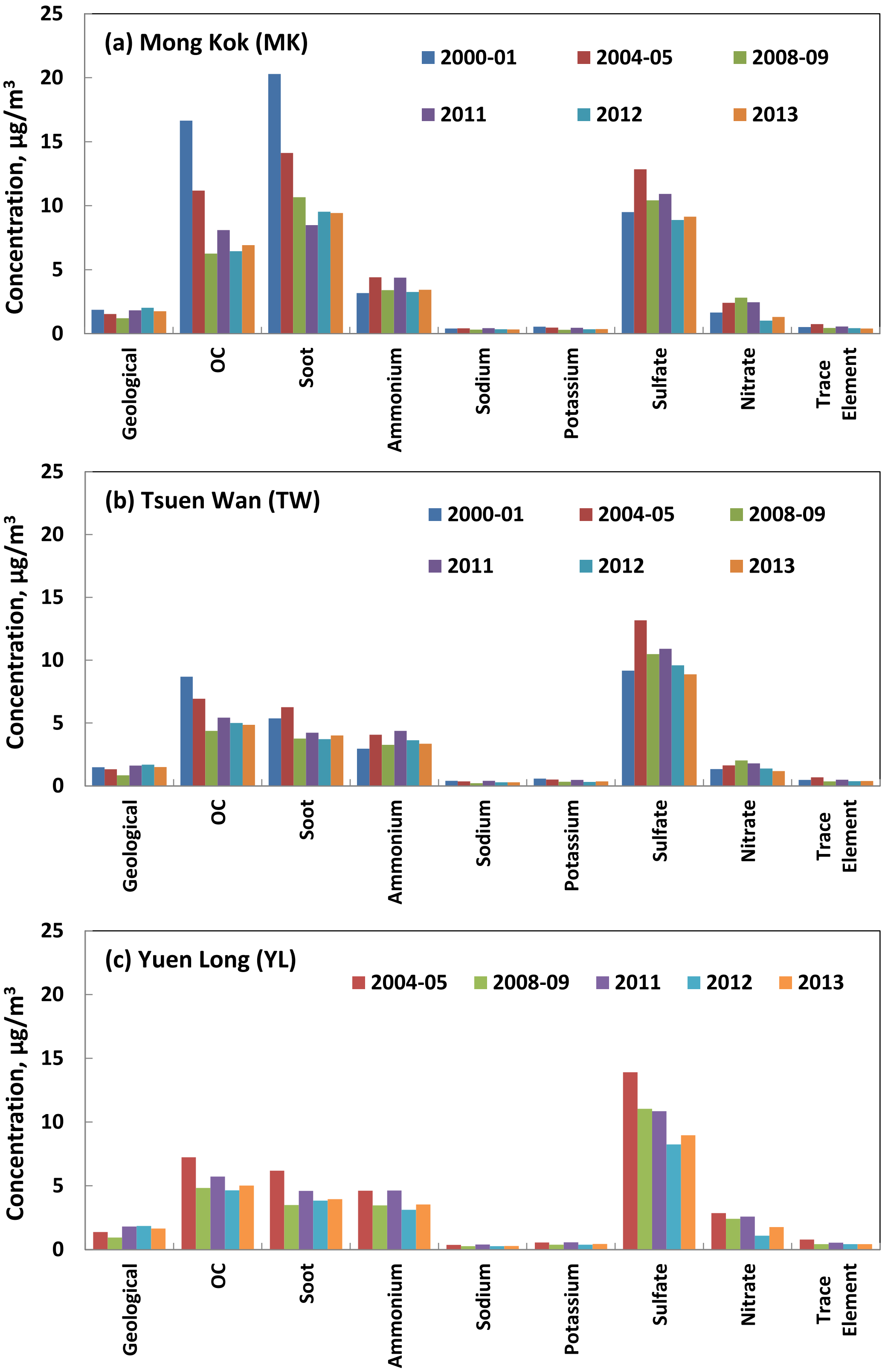


Figure 24. Annual trend of major components of $PM_{2.5}$ samples collected at (a) MK, (b) TW, and (c) YL.

5. Summary

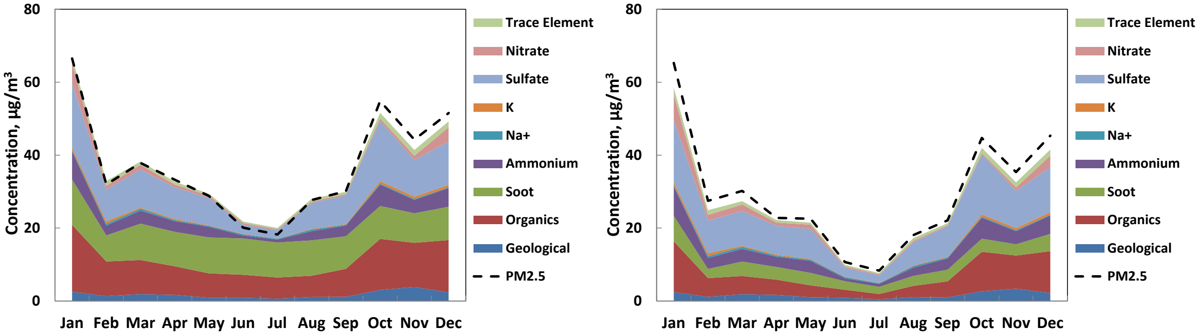
This data summary report covers the validation and quality assurance aspects of the chemical analysis of filter samples from the Hong Kong $PM_{2.5}$ speciation network from January 1 through December 31, 2013. Samplings were conducted at Mong Kok (MK), Central/Western (CW), Clear Water Bay (WB), Tung Chung (TC), Tsuen Wan (TW), and Yuen Long (YL) sites on a 1-in-6 day schedule which yielded a total of 62 sampling events through the year. 1104 filter samples were received by the ENVF/HKUST team for chemical analysis, including 552 Teflon filters and 552 QMA filters.

The valid data rate exceeds 99%. 6 filter samples (5 Teflon and 1 QMA) were flagged as invalid during sampling quality assurance process while 2 QMA filters were flagged as suspected samples during gravimetric analysis. The laboratory accuracy and precision were within limits as demonstrated by routine QC samples.

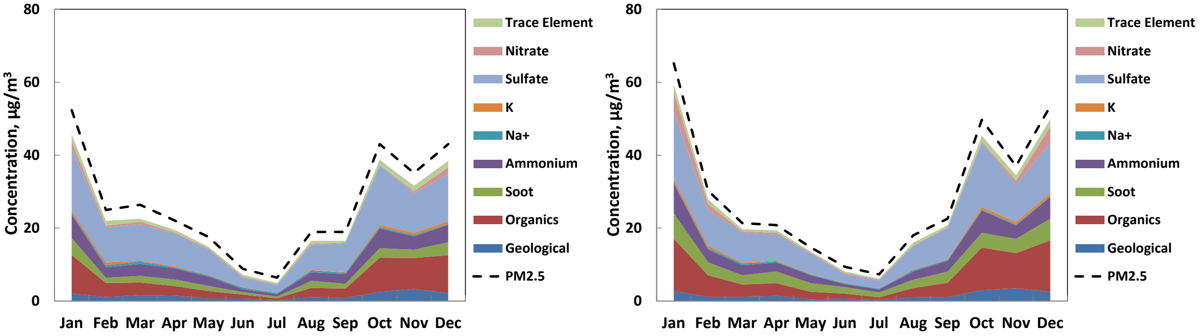
The highest annual average $PM_{2.5}$ concentration of 36.72 $\mu g/m^3$ was measured at the roadside MK site. The lowest annual average $PM_{2.5}$ concentration of 26.08 $\mu g/m^3$ was found at the suburban WB site. The $PM_{2.5}$ concentrations at 5 out of the 6 monitoring sites were within the new AQO annual $PM_{2.5}$ standard of 35 $\mu g/m^3$.

Two levels of validation were performed on the complete dataset. Reconstructed mass and measured mass were highly correlated with correlation coefficients (R^2) ranging from 0.99 to 1.00 at individual sites. It further supports the validity of both gravimetric analysis and chemical measurements. The reconstructed mass averagely explains approx. 92% of the measured $PM_{2.5}$ mass.

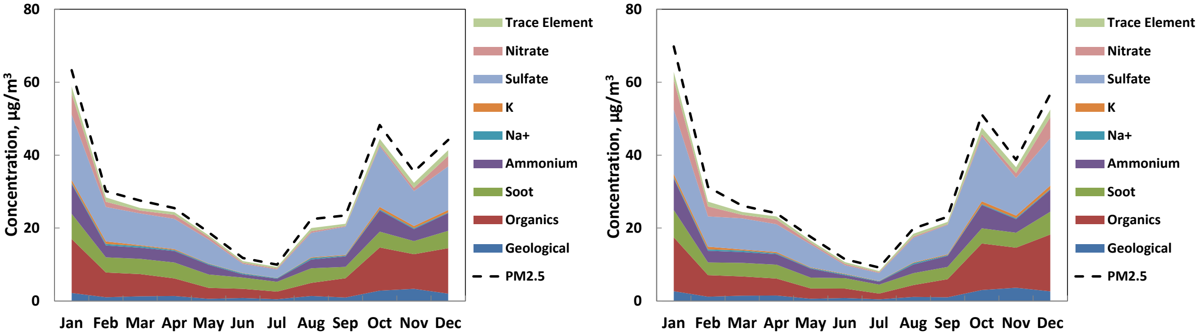
Similar to the past years, sulfate is still the most abundant component in the $PM_{2.5}$ across all the six sites (28.9 - 35.5%). Organic carbon is the second most abundant component with mass contributions ranging from 12.9% at WB site to 18.8% at MK site. It is noted that OC, instead of OM, is discussed here since the conversion factor between OM and OC is empirical and uncertain. Nitrate concentrations were much lower than those of sulfate, contributing 2.2 - 5.7% to the total fine PM mass at all the sites. Ammonium was reasonably balanced by sulfate and nitrate and it was suggested to exist dominantly as ammonium sulfate across all the sampling sites in the year of 2013. EC concentrations exhibited a clear roadside-urban-suburban gradient pattern with highest concentration (9.42 $\mu gC/m^3$, 25.7% of the $PM_{2.5}$ mass) observed at MK site and the lowest concentration (1.96 $\mu gC/m^3$, 7.5% of the $PM_{2.5}$ mass) at WB site.


(a) Mong Kok (MK)

(b) Central/Western (CW)


(c) Clear Water Bay (WB)

(d) Tung Chung (TC)


(e) Tsuen Wan (TW)

(f) Yuen Long (YL)

Figure 25. Monthly average of $PM_{2.5}$ mass concentrations and chemical compositions for (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL during 2013 $PM_{2.5}$ speciation study.

Monthly average $PM_{2.5}$ concentration and chemical composition for individual sites are shown in Figure 25 in order to examine the seasonal trends of the $PM_{2.5}$ constituents. The results showed that Hong Kong experienced higher $PM_{2.5}$ levels during fall and winter months (Jan, Feb, Oct, Nov, and Dec) while summer months (Jun–Aug) usually have lower $PM_{2.5}$ concentrations. The monthly average $PM_{2.5}$ level in Sep. 2013 was similar to those in the summer months. It is very likely due to the heavy rain episodes in this month, as recorded by the Hong Kong Observatory [HKO, 2013].

The annual average concentrations of $PM_{2.5}$ mass and major constituents remained at similar levels to those in the past two years. The clear roadside-urban-suburban gradient pattern of EC concentrations suggested that local sources (e.g. on-road vehicles) were its major contributors. While a wide range of measures taken by the HKSAR Government to control the vehicular emissions were proved to be effective and responsible for the general decreasing trend of EC levels observed at roadside, continuous efforts are in need to further improve the air pollutions so as to meet the new AQO criteria.

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Appendix A. Side-by-side comparison of the six one-year studies of $PM_{2.5}$ samples (in μg/m^3) collected during 2000-01, 2004-05, 2008-09, 2011, 2012, and the current 2013 period. Carbon concentrations (in μgC/m^3) are from the IMPROVE_TOR method.

	2001	2001	2001		2005	2005	2005	2005		2009	2009	2009	2009		2011	2011	2011	2011	2011	2011		2012	2012	2012	2012	2012	2012		2013	2013	2013	2013	2013	2013
	MK	TW	HT		MK	TW	YL	HT		MK	TW	YL	HT		MK	CW	WB	TC	TW	YL		MK	CW	WB	TC	TW	YL		MK	CW	WB	TC	TW	YL
Teflon Mass	58.28	34.12	23.66		53.02	38.59	41.31	28.44		41.60	30.61	31.78	24.10		43.08	35.36	31.32	35.57	35.30	38.22		34.71	29.32	28.75	29.10	31.26	27.95		36.72	28.99	26.08	28.59	29.50	31.01
QMA Mass	62.50	37.28	25.85		54.87	40.75	43.91	29.64		45.92	34.00	36.34	25.94		47.92	39.84	35.89	39.81	40.56	42.89		39.96	34.47	32.60	32.89	35.22	32.01		41.38	33.36	30.38	32.40	33.97	35.37
Cl^-	0.256	0.138	0.143		0.283	0.126	0.264	0.124		0.312	0.175	0.213	0.298		0.205	0.191	0.105	0.109	0.122	0.174		0.108	0.174	0.072	0.088	0.117	0.109		0.119	0.137	0.093	0.093	0.095	0.111
NO_3^-	1.65	1.34	0.71		2.40	1.64	2.86	0.76		2.81	2.03	2.42	1.51		2.45	2.39	0.93	1.90	1.80	2.59		1.01	1.85	0.84	0.95	1.38	1.09		1.31	1.42	0.58	1.16	1.17	1.76
SO_4^{2-}	9.50	9.17	8.64		12.84	13.17	13.91	11.91		10.41	10.48	11.04	9.66		10.91	10.91	11.13	11.09	10.91	10.85		8.88	8.16	9.86	9.82	9.59	8.25		9.14	9.08	9.25	9.08	8.88	8.96
NH_4^+	3.17	2.96	2.16		4.40	4.07	4.62	3.06		3.40	3.27	3.47	2.63		4.37	4.45	4.09	4.38	4.38	4.63		3.25	3.22	3.52	3.51	3.64	3.12		3.42	3.45	3.16	3.40	3.36	3.54
Na^+	0.398	0.397	0.679		0.423	0.362	0.375	0.527		0.320	0.211	0.262	0.380		0.431	0.452	0.510	0.413	0.404	0.402		0.345	0.355	0.359	0.368	0.290	0.275		0.326	0.342	0.401	0.299	0.292	0.278
K^+	0.457	0.492	0.403		0.479	0.486	0.562	0.433		0.278	0.308	0.365	0.259		0.467	0.463	0.483	0.534	0.492	0.590		0.275	0.326	0.336	0.358	0.385	0.276		0.319	0.314	0.318	0.350	0.309	0.385
OC	16.64	8.69	4.23		11.18	6.93	7.23	3.92		6.26	4.38	4.83	2.70		8.09	4.92	3.91	5.13	5.44	5.73		6.45	4.50	4.08	4.12	5.01	4.64		6.92	4.37	3.37	4.27	4.86	5.02
EC	20.29	5.37	1.68		14.12	6.26	6.19	2.28		10.66	3.76	3.49	1.21		8.48	3.71	2.43	3.65	4.24	4.61		9.52	4.41	2.60	2.76	3.72	3.84		9.42	3.48	1.96	3.37	4.01	3.96
TC	36.91	14.04	5.89		25.28	13.18	13.42	6.19		16.91	8.12	8.31	3.89		16.55	8.60	6.31	8.76	9.65	10.31		15.96	8.90	6.67	6.87	8.72	8.48		16.33	7.84	5.33	7.64	8.86	8.97
Al	0.1139	0.1146	0.1094		0.1408	0.1414	0.1448	0.1223		0.0986	0.0828	0.0913	0.0828		0.1942	0.2008	0.1990	0.2009	0.1910	0.2114		0.2365	0.2134	0.2260	0.2322	0.212	0.2368		0.2034	0.2054	0.2005	0.2061	0.1916	0.2115
Si	0.4778	0.3870	0.3489		0.3469	0.3141	0.3221	0.2546		0.2485	0.1853	0.2073	0.1685		0.3981	0.4209	0.3980	0.4079	0.3888	0.4349		0.4393	0.3882	0.4064	0.4175	0.3899	0.4311		0.3732	0.3897	0.3527	0.3604	0.3436	0.3779
P	0.0092	0.0050	0.0028		0.1886	0.1950	0.1917	0.1747		0.0225	0.0237	0.0229	0.0225		0.0194	0.0163	0.0150	0.0158	0.0163	0.0155		0.0211	0.0144	0.0129	0.0140	0.0138	0.0148		0.0177	0.0133	0.0124	0.0121	0.0140	0.0145
S	3.4886	3.3789	3.0534		4.3005	4.5835	4.5622	4.2099		3.3471	3.4305	3.4535	3.1650		3.6677	3.7263	3.8399	3.7518	3.7641	3.7813		3.3455	3.4259	3.1763	3.3431	3.1509	3.2280		3.1377	3.1135	3.2338	3.1359	3.1369	3.0990
Cl	0.1169	0.0874	0.1432		0.1391	0.0758	0.1590	0.0709		0.1037	0.0568	0.0941	0.0799		0.0889	0.1203	0.0720	0.0726	0.0640	0.0774		0.0386	0.0566	0.0235	0.0373	0.0491	0.0621		0.0754	0.0909	0.0954	0.0861	0.0741	0.0788
K	0.5517	0.5858	0.4892		0.4678	0.5080	0.5631	0.4551		0.3064	0.3281	0.3828	0.2780		0.4619	0.4677	0.4740	0.5192	0.4797	0.5722		0.3447	0.3324	0.3005	0.3454	0.3211	0.3882		0.3658	0.3714	0.3690	0.3931	0.3622	0.4366
Ca	0.1705	0.1262	0.1024		0.1082	0.0896	0.0891	0.0652		0.1102	0.0729	0.0738	0.0626		0.1298	0.1209	0.0914	0.0959	0.1006	0.1111		0.1461	0.1072	0.1090	0.1117	0.1253	0.1207		0.1244	0.1088	0.0853	0.0968	0.1053	0.1088
Ti	0.0092	0.0088	0.0079		0.0109	0.0102	0.0114	0.0062		0.0109	0.0084	0.0097	0.0062		0.0128	0.0118	0.0106	0.0138	0.0117	0.0156		0.0147	0.0124	0.0116	0.0147	0.0127	0.0153		0.0126	0.0116	0.0103	0.0128	0.0106	0.0139
V	0.0134	0.0137	0.0117		0.0190	0.0237	0.0195	0.0167		0.0175	0.0182	0.0144	0.0177		0.0146	0.0150	0.0119	0.0139	0.0206	0.0139		0.0197	0.0182	0.0133	0.0140	0.0208	0.0145		0.0219	0.0190	0.0145	0.0143	0.0245	0.0142
Cr	0.0010	0.0009	0.0006		0.0017	0.0015	0.0017	0.0014		0.0014	0.0012	0.0016	0.0011		0.0021	0.0020	0.0022	0.0022	0.0021	0.0024		0.0023	0.0022	0.0019	0.0022	0.0022	0.0022		0.0022	0.0018	0.0017	0.0021	0.0017	0.0020
Mn	0.0128	0.0124	0.0077		0.0170	0.0158	0.0170	0.0123		0.0127	0.0113	0.0127	0.0087		0.0214	0.0214	0.0174	0.0226	0.0186	0.0215		0.0194	0.0168	0.0132	0.0158	0.0163	0.0190		0.0163	0.0168	0.0130	0.0152	0.0156	0.0183
Fe	0.2692	0.1871	0.1219		0.2579	0.1858	0.1996	0.1190		0.2343	0.1325	0.1552	0.0947		0.2958	0.1978	0.1582	0.2094	0.1932	0.2215		0.3051	0.1881	0.1527	0.1959	0.1962	0.2223		0.2779	0.1818	0.1344	0.1777	0.1780	0.2027
Co	0.0001	0.0001	0.0002		0.0001	0.0001	0.0001	0.0002		0.0002	0.0002	0.0001	0.0002		0.0005	0.0005	0.0003	0.0004	0.0003	0.0004		0.0002	0.0001	0.0001	0.0001	0.0001	0.0001		0.0002	0.0001	0.0001	0.0000	0.0001	0.0000
Ni	0.0055	0.0054	0.0047		0.0061	0.0071	0.0068	0.0050		0.0049	0.0052	0.0044	0.0050		0.0050	0.0050	0.0042	0.0048	0.0064	0.0049		0.0065	0.0060	0.0045	0.0048	0.0113	0.0051		0.0068	0.0062	0.0052	0.0051	0.0073	0.0049
Cu	0.0113	0.0090	0.0052		0.0110	0.0104	0.0113	0.0065		0.0210	0.0188	0.0167	0.0169		0.0252	0.0215	0.0225	0.0226	0.0207	0.0234		0.0214	0.0181	0.0177	0.0157	0.0151	0.0167		0.0230	0.0182	0.0203	0.0248	0.0212	0.0378
Zn	0.1794	0.1743	0.1087		0.2399	0.2186	0.2381	0.1727		0.1579	0.1343	0.1600	0.1177		0.2156	0.2364	0.1948	0.2909	0.1936	0.2188		0.1887	0.1598	0.1337	0.1366	0.1704	0.1879		0.1567	0.1452	0.1397	0.1301	0.1501	0.1515
Ga	0.0004	0.0004	0.0005		0.0018	0.0030	0.0024	0.0026		0.0003	0.0004	0.0003	0.0004		0.0003	0.0002	0.0002	0.0002	0.0001	0.0001		0.0001	0.0002	0.0002	0.0001	0.0000	0.0002		0.0000	0.0002	0.0002	0.0000	0.0000	0.0001
As	0.0046	0.0055	0.0042		0.0053	0.0063	0.0084	0.0043		0.0012	0.0010	0.0016	0.0006		0.0043	0.0046	0.0053	0.0050	0.0046	0.0058		0.0030	0.0036	0.0026	0.0032	0.0029	0.0029		0.0035	0.0037	0.0040	0.0042	0.0038	0.0044
Se	0.0021	0.0022	0.0020		0.0003	0.0004	0.0005	0.0004		0.0003	0.0004	0.0004	0.0006		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0001	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
Br	0.0129	0.0127	0.0121		0.0106	0.0099	0.0116	0.0108		0.0172	0.0148	0.0143	0.0174		0.0172	0.0170	0.0190	0.0159	0.0156	0.0171		0.0132	0.0134	0.0160	0.0115	0.0108	0.0122		0.0129	0.0133	0.0158	0.0133	0.0128	0.0133
Rb	0.0036	0.0043	0.0032		0.0020	0.0025	0.0029	0.0019		0.0010	0.0011	0.0015	0.0008		0.0011	0.0013	0.0014	0.0015	0.0014	0.0016		0.0007	0.0008	0.0006	0.0009	0.0006	0.0010		0.0007	0.0006	0.0005	0.0009	0.0006	0.0008
Sr	0.0013	0.0011	0.0011		0.0011	0.0011	0.0015	0.0015		0.0017	0.0019	0.0020	0.0015		0.0030	0.0032	0.0030	0.0027	0.0029	0.0030		0.0018	0.0015	0.0016	0.0016	0.0015	0.0014		0.0020	0.0018	0.0020	0.0018	0.0015	0.0017
Y	0.0001	0.0001	0.0002		0.0004	0.0004	0.0004	0.0003		0.0003	0.0004	0.0003	0.0004		0.0002	0.0002	0.0004	0.0002	0.0003	0.0004		0.0001	0.0001	0.0000	0.0001	0.0001	0.0001		0.0001	0.0000	0.0001	0.0000	0.0001	0.0001
Zr	0.0006	0.0006	0.0005		0.0016	0.0013	0.0007	0.0010		0.0010	0.0008	0.0011	0.0010		0.0006	0.0002	0.0003	0.0004	0.0004	0.0006		0.0014	0.0008	0.0006	0.0008	0.0005	0.0007		0.0004	0.0005	0.0006	0.0008	0.0007	0.0006
Mo	0.0005	0.0005	0.0007		0.0015	0.0011	0.0017	0.0012		0.0007	0.0006	0.0007	0.0005		0.0016	0.0012	0.0011	0.0011	0.0013	0.0009		0.0001	0.0000	0.0001	0.0001	0.0002	0.0001		0.0000	0.0001	0.0000	0.0000	0.0000	0.0000
Pd	0.0012	0.0017	0.0011		0.0019	0.0014	0.0016	0.0020		0.0006	0.0007	0.0008	0.0005		0.0016	0.0018	0.0023	0.0021	0.0019	0.0018		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ag	0.0011	0.0017	0.0014		0.0013	0.0020	0.0018	0.0012		0.0010	0.0007	0.0008	0.0007		0.0003	0.0002	0.0003	0.0002	0.0001	0.0001		0.0000	0.0006	0.0003	0.0003	0.0004	0.0002		0.0003	0.0003	0.0002	0.0004	0.0002	0.0003
Cd	0.0019	0.0023	0.0022		0.0022	0.0021	0.0025	0.0018		0.0008	0.0007	0.0007	0.0005		0.0006	0.0005	0.0005	0.0006	0.0004	0.0007		0.0007	0.0013	0.0007	0.0004	0.0010	0.0008		0.0002	0.0006	0.0005	0.0008	0.0006	0.0004
In	0.0018	0.0020	0.0014		0.0009	0.0010	0.0017	0.0011		0.0005	0.0005	0.0005	0.0005		0.0003	0.0003	0.0005	0.0006	0.0003	0.0002		0.0001	0.0000	0.0000	0.0000	0.0000	0.0001		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sn	0.0188	0.0203	0.0116		0.0131	0.0188	0.0162	0.0084		0.0107	0.0101	0.0100	0.0091		0.0131	0.0122	0.0125	0.0135	0.0120	0.0154		0.0041	0.0038	0.0035	0.0052	0.0032	0.0049		0.0034	0.0045	0.0046	0.0061	0.0059	0.0113
Sb	0.0046	0.0049	0.0038		0.0042	0.0027	0.0039	0.0033		0.0009	0.0009	0.0014	0.0015		0.0080	0.0074	0.0068	0.0075	0.0067	0.0087		0.0005	0.0005	0.0007	0.0007	0.0002	0.0004		0.0005	0.0011	0.0006	0.0004	0.0007	0.0009
Ba	0.0267	0.0170	0.0086		0.0106	0.0081	0.0068	0.0053		0.0031	0.0031	0.0024	0.0026		0.0167	0.0108	0.0087	0.0104	0.0101	0.0108		0.0348	0.0101	0.0127	0.0108	0.0115	0.0205		0.0109	0.0066	0.0048	0.0048	0.0060	0.0119
La	0.0131	0.0087	0.0130		0.0105	0.0081	0.0082	0.0112		0.0036	0.0034	0.0040	0.0053		0.0164	0.0156	0.0146	0.0163	0.0132	0.0165		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Au	0.0003	0.0005	0.0004		0.0003	0.0006	0.0002	0.0003		0.0000	0.0000	0.0001	0.0002		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0002	0.0001	0.0002	0.0002	0.0001		0.0002	0.0002	0.0001	0.0000	0.0001	0.0002
Hg	0.0001	0.0002	0.0001		0.0000	0.0003	0.0001	0.0001		0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Tl	0.0001	0.0001	0.0001		0.0002	0.0001	0.0000	0.0003		0.0000	0.0001	0.0001	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0001	0.0000	0.0000
Pb	0.0664	0.0726	0.0576		0.0478	0.0498	0.0624	0.0432		0.0405	0.0406	0.0437	0.0399		0.0597	0.0604	0.0626	0.0630	0.0599	0.0671		0.0399	0.0397	0.0370	0.0365	0.0346	0.0384		0.0383	0.0394	0.0413	0.0421	0.0374	0.0428
U	0.0001	0.0002	0.0002		0.0013	0.0011	0.0017	0.0018		0.0008	0.0007	0.0007	0.0010		0.0040	0.0035	0.0040	0.0038	0.0038	0.0035		0.0001	0.0000	0.0000	0.0000	0.0001	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000